

Vol. 25, No. 2, March-April, 1990

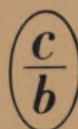
November, 1990

LITHOLOGY AND MINERAL RESOURCES

ЛИТОЛОГИЯ И ПОЛЕЗНЫЕ ИСКОПАЕМЫЕ

(LITOLOGIYA I POLEZNYE ISKOPAEMYE)

TRANSLATED FROM RUSSIAN



CONSULTANTS BUREAU, NEW YORK

LITHOLOGY AND MINERAL RESOURCES

Lithology and Mineral Resources is abstracted or indexed in *Chemical Abstracts*, *Engineering Index*, and *Metal Abstracts Index*.

Lithology and Mineral Resources is a translation of *Litologiya i Poleznye Iskopaemye*, a publication of the Academy of Sciences of the USSR.

An agreement with the Copyright Agency of the USSR (VAAP) makes available both advance copies of the Russian journal and original glossy photographs and artwork. This serves to decrease the necessary time lag between publication of the original and publication of the translation and helps to improve the quality of the latter. The translation began with the first issue of the Russian journal.

Editorial Board of *Litologiya i Poleznye Iskopaemye*:

Editor: V. N. Kholodov

Associate Editors: B. M. Mikhailov and P. P. Timofeev

Secretary: G. Yu. Butuzova

A. N. Dmitrievskii	A. A. Migdisov	E. F. Shnyukov
A. V. Il'in	I. O. Murdmaa	S. A. Sidorenko
V. I. Kononov	V. I. Sedletskii	I. I. Volkov
A. I. Konyukhov	E. M. Shmarinovich	O. V. Yapaskurt

Copyright © 1990, Plenum Publishing Corporation. *Lithology and Mineral Resources* participates in the Copyright Clearance Center (CCC) Transactional Reporting Service. The appearance of a code line at the bottom of the first page of an article in this journal indicates the copyright owner's consent that copies of the article may be made for personal or internal use. However, this consent is given on the condition that the copier pay the flat fee of \$12.50 per article (no additional per page fees) directly to the Copyright Clearance Center, Inc., 27 Congress Street, Salem, Massachusetts 01970, for all copying not explicitly permitted by Sections 107 or 108 of the U.S. Copyright Law. The CCC is a nonprofit clearinghouse for the payment of photocopying fees by libraries and other users registered with the CCC. Therefore, this consent does not extend to other kinds of copying, such as copying for general distribution, for advertising or promotional purposes, for creating new collective works, or for resale, nor to the reprinting of figures, tables, and text excerpts. 0024-4902/90/\$12.50

Consultants Bureau journals appear about six months after the publication of the original Russian issue. For bibliographic accuracy, the English issue published by Consultants Bureau carries the same number and date as the original Russian from which it was translated. For example, a Russian issue published in December will appear in a consultants Bureau English translation about the following June, but the translation issue will carry the December date. When ordering any volume or particular issue of a Consultants Bureau journal, please specify the date and, where applicable, the volume and issue numbers of the original Russian. The material you will receive will be a translation of that Russian volume or issue.

Subscription (6 Issues):

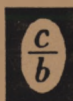
Vol. 24: \$855 (domestic); \$990 (foreign)

Single issue: \$150

Vol. 25: \$915 (domestic); \$1060 (foreign)

Single Article: \$12.50

CONSULTANTS BUREAU, NEW YORK AND LONDON



233 Spring Street
New York, New York 10013

Published bimonthly, consisting of Volume 24 issues 3 through 6 and Volume 25 issues 1 and 2. Subscription price for Volume 24 is \$855, and for Volume 25 is \$915. Second-class postage paid at Jamaica, New York 11431.

Mailed in the USA by Publications Expediting, Inc., 200 Meacham Avenue, Elmont, NY 11003.

POSTMASTER. Send address changes to *Lithology and Mineral Resources*, Plenum Publishing Corporation, 233 Spring Street, New York, NY 10013.

LITHOLOGY AND MINERAL RESOURCES

A translation of *Litologiya i Poleznye Iskopaemye*

November, 1990

Volume 25, Number 2

March-April, 1990

CONTENTS

Engl./Russ.

Lower Cretaceous Halogenous Formations of Central Asia - V. I. Sedletskii and A. A. Baikov	93	3
Lithotypes of Potassium-Bearing Formations - S. M. Korenevskii	99	13
Occurrence Forms and Distribution Balance of Indicator Elements in Tin-Bearing Placers - N. G. Patyk-Kara, L. P. Dolgopolova, and L. I. Serdobova	107	23
Mass Balance in the Sedimentary Cycle of Krivoi Rog Basin Iron Deposits - D. A. Kulik and V. V. Pokalyuk	117	36
Isotopic Composition and Origin of Carbonate Manganese Ores of the Mangyshlak Deposit - V. N. Kuleshov and Zh. V. Dombrovskaya	128	50
Conditions Surrounding the Formation of Stratiform Zeolite Deposits - V. I. Gugushvili, Ts. Sh. Kargareteli, and K. I. Omiazde	139	63
Geologic Models of Gas Hydrate Formation - G. D. Ginsburg and V. A. Solov'ev	150	76
Stromatolitic Nature of Siliceous Horizon in the Chulaktausk Suite of Malyi Karatau - T. V. Litvinova	160	88
Fragments of Quartz, Granitoids, and Metamorphites in Middle Paleozoic Sedimentary Sequences of the Southern Urals - E. A. Belgorodskii	167	97
Lithologic Criteria for Prediction of Authigenic Sulfur Deposits in Halogenous Formations - V. F. Polkunov	173	105
METHODS		
Determination of Illite Crystallinity - N. V. Logvinenko	180	136
OBITUARY		
Dmitrii Gavrilovich Sapozhnikov	182	142

The Russian press date (podpisano k pechati) of this issue was 3/15/1990. Publication therefore did not occur prior to this date, but must be assumed to have taken place reasonably soon thereafter.

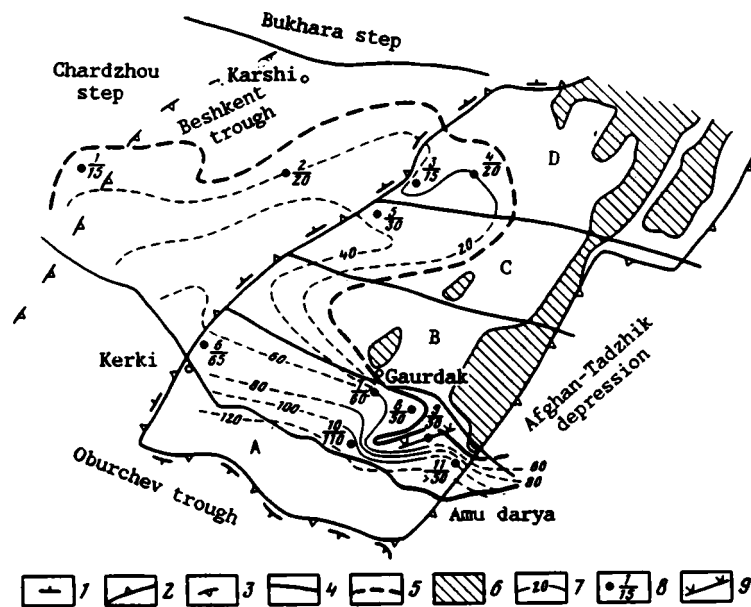


Fig. 1. Lower Cretaceous salt sediments in southwestern Ghissar and Beshkent (cis-South-Ghissar) foredeep: 1-5) boundaries (1 — platform and epiplatformal orogenic region; 2) — southwestern Ghissar anticline; 3) — Beshkent (cis-South-Ghissar) foredeep; 4) — sublatitudinal steps and corresponding troughs (A — Karlyuk, C — Dekhkanabad) and elevations (B — Gaurdak-Kugitanga, D — Baisun-Lyangar); 5) Lower Cretaceous halogenous formation); 6) exposures of subsalt Paleozoic and Mesozoic beds on the day surface; 7) lines of equal thickness of salt member; 8) areas where the Lower Cretaceous halogenous formation is penetrated by drillholes or exposed (numerator = area number; denominator = salt layer thickness, m) (1 — Sunduklin, hole 1; 2 — Alyaudunau; 3 — Karail; 4 — Adamtash, hole 1; 5 — Belesyaninak; 6 — Kerkidag, hole 6; 7 — Tagarin, hole 708; 8 — Karabil, hole 95; 9 — Karlyuk, hole 77; 10 — Kundalyang, hole 1; 11 — Okuzbulak); 9) reflected wave seismic profile.

The Lower Cretaceous rocks that, up the section, supersede a thick Upper Jurassic salt-bearing formation consist of red rock layers; in the southwestern spurs of the Ghissar ridge this bed was subdivided by Kheraskov [14] into several suites (top to bottom): the Karabil suite (consisting of clay, siltstone, and sandstone), the Almuradian suite (mainly clayey, with gypsum and dolomite beds), and the Kyzyltash suite (clayey-silty). Red deposits conform to this structure in piedmont areas, where their overall thickness is about 500 m. This pattern is consistently preserved on a long stretch along the slopes of the Pamir, the Ghissar ridge, and, further west, on the southern margin of the Turanian Plate. Various lithologic and geophysical benchmarks are traceable in the red rocks. They include a 1-6 m dolomite layer with brachiopods and remains of sea urchins and other organisms found in the middle portion of the Almuradian suite and clearly seen on well-logging charts (see Fig. 2).

According to geologic-geophysical data, this sectional pattern is not maintained throughout the territory. As structures subside, the red rock bed grows in thickness and experiences facies alternations that lead to salt deposition. The salt bed appears between a gray-green dense dolomite layer of the Almuradian suite and the overlying gypsum layers (see Fig. 2).

As noted earlier, the increasing thickness of the Mesozoic sediments is closely related to the tectonic build of the territory. In southwestern Ghissar, the Jurassic and Cretaceous increase in thickness toward step-depressions. The Baisnutau-Lyangar and Gaurdak-Kugitanga latitudinal steps were relatively elevated, while the Karabil and Dekhkanabad steps were relatively lowered (see Fig. 1). The general westward tilt of the basement of the southwest Ghissar meganticline toward the Beshkent (cis-South-Ghissar) trough was also responsible for the considerable in-

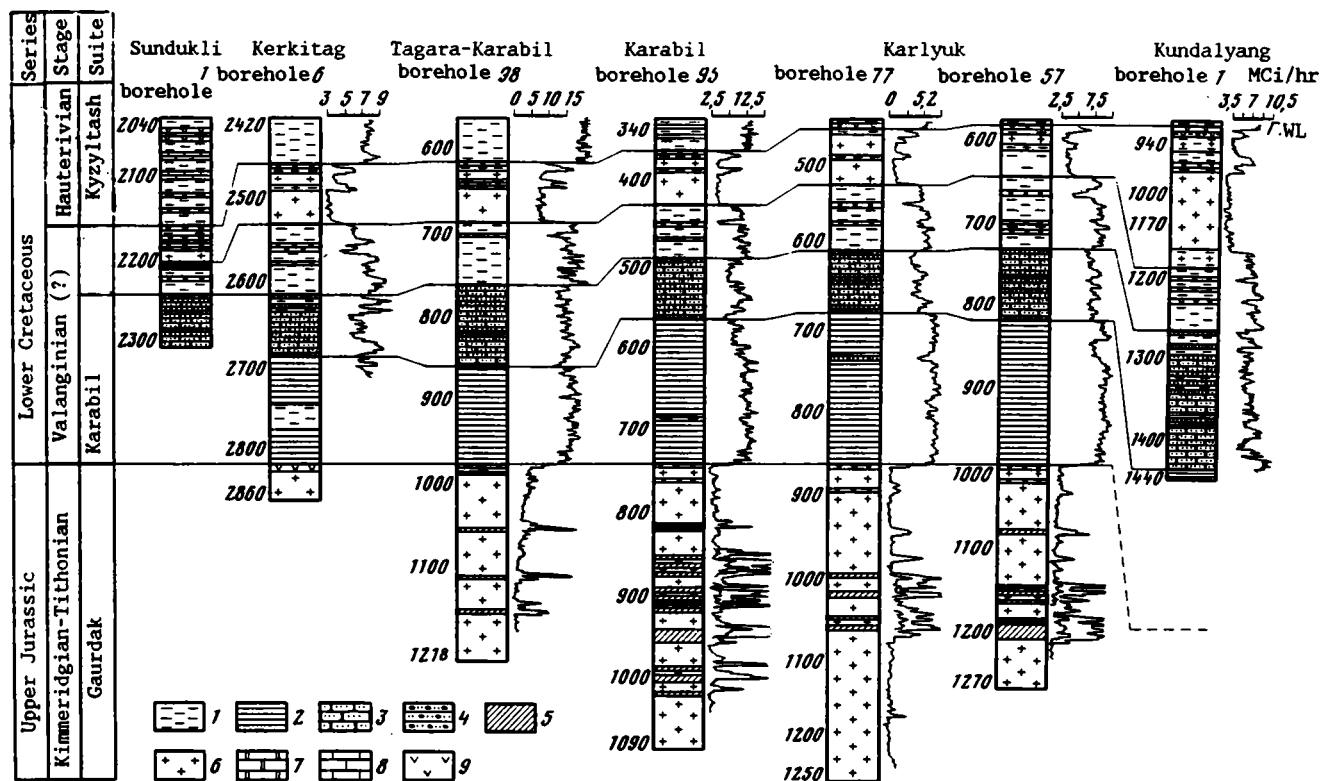


Fig. 2. Correlation of Lower Cretaceous and Upper Jurassic sections of salt deposits in the southwestern Ghissar (after [9]): 1) clays; 2) argillites; 3) sandstones; 4) conglomerates; 5, 6) potash salt and rock salt, respectively; 7) dolomites; 8) limestones; 9) anhydrites.

crease of Mesozoic thickness from east to west. The Cretaceous formations grow in thickness from 500 to 700 m over a stretch of 8 km. The area of the greatest sagging in the Beshkent trough lies along the line of the Lyangar-Kerkidag folds [11].

During the accumulation of Cretaceous sediments, the Afghan-Tadzhik depression was also an area of intense sagging. There are grounds to assume that the thickness and facies of sediments of that age in that territory should also vary greatly toward the center of the depression.

The variation of Cretaceous thickness and facies can be traced on data from drilling and geophysical exploration of the subsided area of the Karlyuk potash salt deposit (Fig. 3). A section in the Karlyuk trough explored by the refracted wave correlation method has a velocity differentiation that allows geophysical prospecting to be conducted on four refracting seismic boundaries. The stratigraphic position of these boundaries (bottom to top): corresponds to the following elements: the base of the Upper Jurassic salt bed (contact with underlying anhydrites); the roof of the Upper Jurassic salt bed (contact with red formation of the Karabil suite); the Lower Cretaceous salt-bearing strata of the Almuradian suite; the surface of the Mesozoic — base of the Quaternary sediments. The refracting seismic boundary associated with salt-bearing sediments of the Almuradian suite was isolated long before these sediments were reached by boreholes. By drilling deep holes it was determined that a new horizon — a salt-bearing Aluradian bed 60–70 m thick — indeed appears amid Neocomian red formations. As everywhere, facies variation is observed against a background of a substantial increase in the thickness of Jurassic and Cretaceous sediments. For example, on the Karlyuk deposit the sediments (including the Almuradian, Karabil, and the salt component of the Gaurdak suite) total at most 900–1000 m; must 8–10 km to the southwest the thickness grows by a factor of 1.5, to 1500 m. The thickness is mostly built up by halogenous formations of both salt-bearing strata.

The Lower Cretaceous salt sediments have been studied most in sections south of the Karlyuk deposit (Kundalyang and Okuzbulak structures), where they are 100–120 m thick. In the northern part of the meganticline the Almuradian salt sediments have been uncovered by many boreholes on Karail, Adamtash, Belesayinak, and other folds; they consistently contract to a thickness of 10–30 m. The main features in the structure of the salt member and its position in the Neocomian section overlying an Almuradian dolomite bed remain unchanged.

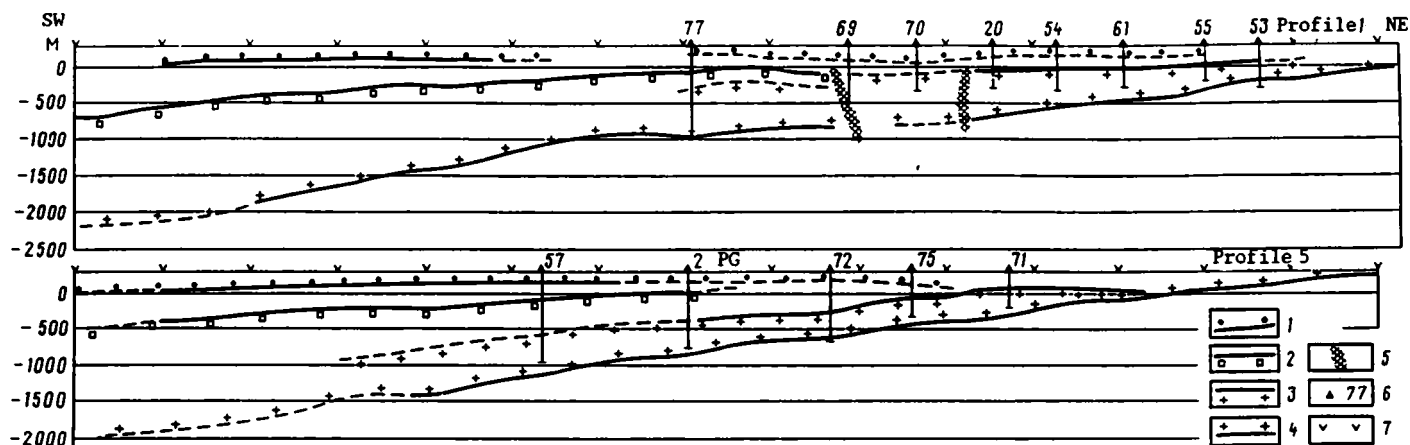


Fig. 3. Reflected wave seismic sections in the Almurad salt bed area of the Karlyuk potash salt deposit (after Sungurov, modified): 1-4) refracting seismic horizons (1 — base of Quaternary rocks; 2 — salt bed of Almuradian suite, Lower Cretaceous; 3 — roof of Upper Jurassic salt bed; 4 — base of Upper Jurassic salt bed (contact with underlying anhydrites)); 5) disruptive faults; 6) borehole and its number; 7) explosion location.

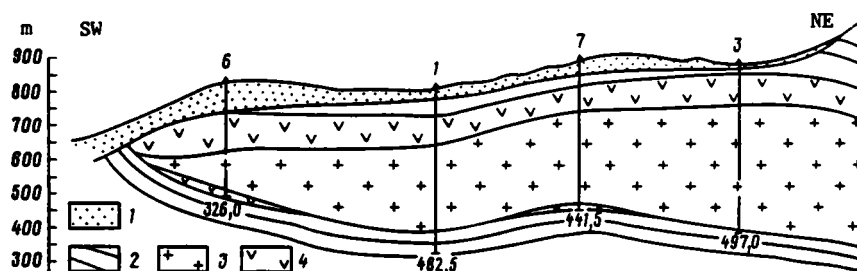


Fig. 4. Geologic section of Tutbulak rock salt deposit (after Vaulin): 1) Ilyak complex (Middle Quaternary); 2) red rocks of the Java suite (Neocomian); 3) rock salt; 4) anhydrites, gypsum.

The Lower Cretaceous in the Beshkent trough has been found at depths usually greater than 2500 m. The salt bed on the Sunduklin anticline is at most 10-12 m thick; on the Alyaunduntau gold it is some 20 m thick. To the south, on the Kerkidag structure, salt layers grow to 70 m. One is struck by the perfect comparability of sections despite the distances of hundreds of kilometers separating them and the fact that they belong to different tectonic structures. As before, a dolomite layer remains a typical marker horizon (in addition to other markers).

Two potash-bearing salt strata occur amid the Gaurdak and Almuradian rocks on the area of the Okuzbulak deposit [12]. The Upper Jurassic Gaurdak salt bed emerges to the layer underlying the Quaternary in the arch of the Aktag anticlinal fold. The upper potash-bearing salt member (according to drilling) is some 270 m thick; the total thickness of the salt-bearing bed is over 500 m. We identified up to 11 layers, lenses, and interlayers of sylvinitic potash salts in the potash-bearing member; these layers are thick and have a high KCl content. In the section they alternate with layers of pink rock salt. The salt section of the Gaurdak suite ends at a clayey anhydrite layer 4-13 m thick, which makes a gradual transition to the overlying rocks.

A bed of Lower Cretaceous red rocks lies over the roof of the Upper Jurassic halogenous formations. At the base this bed consists of clays, sandstones, and siltstones of the Karabil suite over 200 m thick. It is overlain by fine-grained red rocks with interlayers of gypsum and dolomite and Almuradian salt sediments. The Lower Cretaceous salt bed is exposed along the regional Kugitanga-Baisuntau fault, at the foot of the Aktag mountain range formed by overlying red Neocomian rocks that make up the southern side of the Aktag fold. Rock salt contains numerous inclusions, interlayers, and lenses of dark-red sylvinites; locally, sylvinites form stratal deposits consistent to the strike. The visible thickness of the salt bed adjusted for the sloping mine is approximately 50 m. According to Shugin [16], two beds of clayey salt are identified as potash-bearing horizons: the lower bed of 2.5 m with average KCl content close to 22%, and the upper 4-m thick with a KCl content of 16.3%. There is a minor magnesium chloride admixture. Insoluble residue content varies from 5 to 15% and more.

The salt bed is overlain by a typical horizon that can also be traced clearly in sediments that contain no Lower Cretaceous salt. It is a bed of primary sedimentary breccia-like, offblue-gray and brown clays, up to 8 m thick, known as desiccation breccias. They are overlain by an 8-10 m thick bed of gray clay gypsum, which is followed by a set of rhythmic interstratified clay, silt, and sandstone layers of the Kyzyltash suite, 150 m thick. Up the section it gives way to lagoonal and normal-marine sediments.

According to detailed geologic surveys, the salt bed occurs conformably to the overlying sediments. The contact with the salt and overlying breccia-like clays and gypsums and between the gypsum and red rocks covering it is a normal stratigraphic contact without any traces of dragging, rupture, or angular discontinuities.

The Upper Jurassic age of the salt bed exposed on Okuzbulak is based on two considerations. First, before large-scale drilling and geologic surveying it was thought impossible that any salt could exist in the Almuradian suite. Second, the salt bed is not completely exposed, and marker dolomites are known at some distance from salt outcrops. Determining the stratigraphic characteristics of the salt was therefore difficult. This gave rise to the theory that the Okuzbulak exposure of the rock it belongs to the Gaurdak suite and is associated with a tectonic fault on which these salts come in contact with red rocks of the Almuradian and Kyzyltash suites. Later it is determined that, although a fault does exist there (the Kugitanga-Baisuntau fault), it lies to the north of the salt outcrop and not to the south, as was believed previously, and is overlain by thick Neogene-Quaternary alluvial stratum, which, in turn, overly Gaurdak salts.

The salt-bearing Almuradian suite section is remarkable. Halogenous layers are overlain and underlain by thick red terrigenous rock formations that developed in continental settings, in shallow lagoons or in freshwater basins, as evidenced by finds of freshwater fauna. The halogenous section lies on a primary sedimentary limestone bed (dolomite horizon) with normal marine fauna (coral colonies, rudists, brachiopods, and sea urchins) typical for shallow basins.

Unlike the underlying Upper Jurassic salt, this salt bed has a distinct seasonal stratification or striation. It includes a considerably amount of terrigenous matter; the clay interlayers are interstratified with rock salt and anhydrite.

Intraformational breccia is another lithologic-bathymetric characteristic indicating that the salt bed was formed in a shallow setting. Along the course of the Almuradian suite the breccia zone gradually replaces the salt layer; it is traceable over a dolomite bed of the Almuradian suite as lenses and interlayers up to 5 m thick. It consists of fragments of light-gray fine-layered argillites and red rocks cemented by a brown clay mass and anhydrite. The origin of this breccia is clearly related to wave and surf action that destroyed lithified sediment accumulated in the shallow basin. The fact that the Almuradian salt basin was shallow in the southwestern spurs of the Ghissar ridge is confirmed by the meandering contour of the coastline and the absence of salt within the Almurad and anticlinal folds, situated between boreholes 77 and 95 (see Fig. 1). Yet, the shallowness of the Almurad salt basin cannot explain the peculiar structure of the salt deposit section. The salt bed lies mainly in the middle portion of a thick red terrigenous formation. Subsalt carbonate sediments are absent (not counting the dolomite bed). Even more remarkable, there is no bed of subsalt sulfate deposits in this section. On the other hand, the salt strata that include potash salt beds and a cover anhydrite layer partly separated from the salt by a clay interlayer contain a remarkably high amount of clays. All Lower Cretaceous salts typically have a very low bromine content (bromine is a characteristic trace element of marine salt-bearing sediments). On average, the amount of bromine is lower by an order of magnitude than in the Upper Jurassic halogenous deposits [13], apparently due to the diluting effect of water from land that also brought clay material into the deposit.

All these features can be accounted for by the fact that we drilled and studied marginal parts of a salt-bearing basin, remote from its supply province. This zone probably received well-prepared brines that gave rise to the halogenous process, despite the abundant clay matter received from the land. In the central parts of that basin, one should then expect not only thicker Lower Cretaceous salt sediments but also the occurrence of carbonate and sulfate members. Nor should the potash-bearing interval of the section remain unchanged. At the center of the basin we expect a great thickness of potash beds and a lower content of clay matter in them. Because of the geological structure of this region, it is impossible to reach potash-bearing deposits at depths of 1200-1500 m. It is unlikely that this basin will be of any commercial importance for potash mining in the near future.

The potash prospects of the Lower Cretaceous are not the only practical aspect of this issue. Importantly, in the central part of the Khiva-Murgab depression the presence of a Lower Cretaceous salt bed enhances the probability of gas finds in the Lower Cretaceous subsalt complex that could have perfect collector qualities. We recommend that exploratory drilling be conducted in that promising area in the near future.

An additional point should be made: given the similarity of the geological build of Mesozoic sediments in the Khiva-Murgab and Afghan-Tadzhik depressions, a salt-bearing bed is not to be ruled out in the section of the Almuradian suite in the central part of the Afghan-Tadzhik depression and in its western part, bordering on southwestern Ghissar. Salt deposits in sections of different tectonic structures have been reported as covered and underlain by Lower Cretaceous red formations. For instance, in the western part of the Afghan-Tadzhik depression, exposed salt deposits with a bed of sedimentary cover anhydrite at the roof, are overlain by a Neocomian red layer with a normal stratigraphic contact. Lower Cretaceous red formations have been also uncovered by boreholes in the salt bed of the Tutbulak rock salt deposit in the near-arch part of the western side of the Karatau anticline. The geological structure of this deposit is typical (see Fig. 4).

The rock salt bed is covered conformally and underlain by terrigenous Lower Cretaceous red formations (Java suite). The salt deposit forms a bed. Finely stratified anhydrite occurs above the roof and inside the 400-m-thick rock salt formation. Stratification and striation, clearly seen in the salts, are oriented according to the bedding of anhydrites and red rocks.

In Shvanov's stratigraphic scheme [15], the Java suite is correlated with the Almuradian suite and upper part of the Karbil suite of the southwestern spurs of the Ghissar ridge.

A bed amid Lower Cretaceous, mainly red rocks, formations has been found in the Nurek rock salt deposit; it is exposed 70 km southwest of that location at the Sharituz deposit and in other areas. Most investigators, presuming that halogenous rocks are of an Upper Jurassic age, were forced to resort to fault tectonics, especially low-angle overthrusts, to explain the occurrence of salt deposits amid red rocks.

Kuznetsova and Vaulin [5] report that the Nurek salt deposit has tectonic contacts with the surrounding rocks (Lower Cretaceous) and consists of anhydrites and Upper Jurassic rock salt (Kimmeridgian-Tithonian age). Popov et al. [6], in describing Tutbulak salts, mention a major low-angle tectonic overthrust along which the halogenous Upper Jurassic bed is shifted over Lower Cretaceous rocks. However, they fail to explain the fact that, despite the great distance separating these areas, the effect of the overthrusts in each case had the same result: the salt bed was enclosed amid Lower Cretaceous red formations. This alone brings into doubt such tectonic reconstructions. For instance, Sadykov [7] follows them unreservedly to classify the salt sections of Nurek and Karatau as Lower Cretaceous.

The signs of salt tectonics in the Afghan-Tadzhik depression as well as the Khiva-Murgab depression appear to be local. For instance, in the Kulyab region (eastern part of the depression) distinct diapir structures break through Mesozoic and Cenozoic rocks, and salt beds occur on layers of different age up to the Quaternary. This seems to be a phenomenon of a different geologic nature, which cannot be extended by analogy to the entire territory of the depression.

It appears essential to revise the conventional tectonic schemes of the Afghan-Tadzhik depression to incorporate the new data presented in the present paper. These data can easily be verified by drilling and by comparison with primary geophysical data from southwestern Uzbekistan and southeastern Turkmenia. Studies of Lower Cretaceous potash-bearing formations, unique in the territory of the USSR, should be continued during the course of prospecting for oil and gas in southern Central Asia.

LITERATURE CITED

1. M. M. Aliev, V. V. Drushits, N. A. Krylov, et al., *The Lower Cretaceous of the Southern USSR* [in Russian], Nauka, Moscow (1985).
2. A. A. Baikov, "New data on salt tectonics of the southwestern Ghissar," *Dokl. Akad. Nauk SSSR*, 256, No. 3, 654-657 (1981).
3. É. A. Vysotskii, R. G. Garetskii, and V. Z. Kislik, *Potassium Basins of the World* [in Russian], Nauka i Tekhnika, Moscow (1988).
4. V. S. Luchnikov, "Upper Jurassic halogenous formation of southeastern Central Asia," in: *Structures of Sedimentary Formations* [in Russian], Nauka, Novosibirsk (1982), pp. 19-33.

5. A. I. Kuznetsova and V. A. Vaulin, "Geological structure and chemical composition of salt-bearing strata in the Nurek rock salt deposit," *Izv. Akad. Nauk TadzhSSR, Otd. Geol., Khim. Tekhn. Nauk.*, No. 4 (13) (1963).
6. V. S. Popov, T. S. Sadykov, M. V. Igonina, and G. P. Morozova, "The rock salt deposit at Tutbulak," *Byul. Nauch.-Tekhn. Inform. Gosgeolkomiteta SSSR*, No. 2 (52) (1964).
7. T. S. Sadykov, "Lithofacies features of the halogenous formation of southwestern Tadzhikistan," in: *New Data on the Geology of Salt Basins in the USSR* [in Russian], Nauka, Moscow (1986), pp. 43-52.
8. V. I. Sedletskii, "Features of salt tectonics of the Gaurdak-Kugitanga region," in: *The Tectonics of Turkmenia* [in Russian], Nauka, Moscow (1966), pp. 107-113.
9. V. I. Sedletskii, "New data on salt-bearing sediments in the Khiva-Murgab depression and the southwestern Ghissar meganticline," *Geol. Nefti Gaza*, No. 9, 29-34 (1970).
10. V. I. Sedletskii and A. A. Baikov, "Lower Cretaceous salt sediments in Central Asia," in: *Geology and Potassium Prospects of the Siberian Platform and Other Salt Accumulation Regions in the USSR* [in Russian], Nauka, Moscow (1970), pp. 252-254.
11. V. I. Sedletskii and A. A. Baikov, "On the formation time of the southwestern Ghissar meganticline and the Beshkent trough," *Byul. MOIM, Otd. Geol.*, 4, 54-61 (1972).
12. V. I. Sedletskii and V. V. Gerasimova, "Rock salt and potash salt," *Geology of the USSR*, Vol. 22: Turkmenia: [in Russian], Nedra, Moscow (1984), pp. 220-232.
13. V. I. Sedletskii and V. S. Derevyagin, "Distribution of bromine in Mesozoic salt sediments in Central Asia and their correlative significance," *Dokl. Akad. Nauk SSSR*, 185, No. 1, 185-187 (1969).
14. N. P. Kheraskov, "Exploration in the search for potassium in Central Asia (geologic exploration in the southwestern extremity of the Ghissar ridge)," *Gaurdanskii Khimicheskii Kombinat*, 2, Part 1 (1934).
15. V. N. Shvanov, "Types of sections and stratigraphy of the Lower Cretaceous of western Tadzhikistan," *Izv. Akad. Nauk TadzhSSR, Otd. Geol., Khim. Tekhn. Nauk.*, No. 1 (3), 69-86 (1961).
16. A. A. Shugin, "Results of exploration of the Okuzbulak potassium deposit," *Tr. Nauchn. in-ta po Udobreniyam i Insektofungisidam*, Issue 138 (1937).

LITHOTYPES OF POTASSIUM-BEARING FORMATIONS

S. M. Korenevskii

UDC 553.632

A lithologic typology of potassium-bearing formations is suggested. Three lithotypes are defined: chloridic, sulfate-chloridic, and sulfatic. Each is characterized by a specific set of minerals.

Potassium-bearing formations are usually defined as those halogenous formations that contain commercial deposits of potassium salts or potassium-magnesium salts. Of all the halogenous strata, these formations are represented most completely in sections. They include a variety of evaporitic rocks. Salt accumulation cycles are completed by the precipitation of high-soluble potassium salts and even magnesium salts. Potassium formations are often referred to as halogenous formations of a complete profile or complete sections [13].

Several attempts have been made recently to develop a typology of halogenous formations, including the potassium-bearing ones. Zharkov [9] created a detailed scheme, but it was too fragmentary to be convenient for field diagnostics or for practical use by geologists. Geologists in the field continue to operate with simple versions of potassium formation classifications.

One such commonly used typology of potassium formation was suggested in [13, 14]. It rests on a lithologic principle where the type of formation is determined by some lithologic properties but not by the entire set of lithologic characteristics; rather, only the lithology of the final portions of salt accumulation cycles and the compo-

All-Union Geological Research Institute, Leningrad. Translated from *Litologiya i Poleznye Iskopaemye*, No. 2, pp. 13-22, March-April, 1990. Original article submitted August 14, 1989.

sition of potassium and magnesium salts are considered. The fact that potassium salt and potassium—magnesium salt deposits are the most valuable commercial resource among potassium formations has nothing to do with this choice. In a natural environment, the mineral variety composition of these easily soluble salts was controlled not only by the conditions of salt accumulation [1] that created formations with specific sets of lithologic sections, but was also prepared by the settings where individual lithologic complexes of the subsalt section were formed, i.e., the lithochemistry of land masses (supply provinces) surrounding the halogenous basins.

Data on the best-studied sections (already explored or actually being mined) of potassium formations of the world [6, 8, 11, 13, 23] indicate that there are three types of mineral composition of potassium salts and potassium—magnesium salts: chloridic, sulfate-chloridic, and sulfatic. Sylvinite and carnallite rock deposits are typical for chloridic potassium formations. Sulfidic-chloridic deposits also include layers of bischofite and sulfuric acid potassium—magnesium salts: kainite, langbeinite, polyhalite, and kieserite, as well as deposits of multimineral rocks, such as hartsalz. Borates are typical for this kind of formation. Locally, magnesite is found amid intraformational carbonate rocks. Sulfatic potassium formations have mainly kainitic and langbeinitic rocks containing potassium—magnesium salt deposits; they also include hartsalz, small sylvinite lenses, and polyhalite rock interlayers. Sections of this type are depleted of anhydrite and carbonate rocks and enriched in terrigenous matter.

The specific processes that formed the lithologic attributes for each type of potassium formation were also determined by the nature and evolution of subsalt strata. Chloridic potassium formations are usually underlain by sulfate-chloridic carbonate beds — both carbonaceous and terrigenous; sulfatic formations are underlain only by terrigenous rocks. The types of potassium formation depend on the effects of the sea and the surrounding land masses, which shaped the conditions in the potassium basin. Chloridic potassium formations suggest a predominant role of the sea, with carbonate accumulation replaced by precipitation of calcium sulfates and then chlorides; for the sulfatic sets the influence of continental waters was more significant.

There are over 30 known potash-bearing formations on the globe [8, 11], including 10 in the USSR [6, 13, 23]. Chloridic and sulfate-chloridic types are predominant, while sulfatic types are almost unique. During geologic time, the evolution of potassium formations proceeded in a certain direction [9, 15]. It was associated with the growth of continents and the changing composition of continental discharge waters and ocean waters. Chloridic potassium formations developed before the Permian. During the Permian, they were joined by sulfate-chloridic formations. During the Triassic and Jurassic-Cretaceous, chloridic potassium formations continued to accumulate. The Neogene favored sulfatic formations.

The pre-Permian, with its powerful carbonate buildup, was a time when salt accumulated in the sea. Subsequently, evaporite formation became affected by continental water (periodically or locally). This effect was most pronounced in the lithology of Neogene potassium formations, which include a lot of terrigenous matter and minerals (mirabilite, glauberite, etc.) typical for continental halogenous formations. These minerals (as well as thenardite) appear in some sulfate-chloridic formations as well, but in much smaller amounts.

The salt composition of brines in basins that later produced potassium deposits was prepared over a long period of time, even before they became salinized. This process was largely controlled by the predominance of marine or continental supply sources in the presalt basins and continued to influence salinization and salt accumulation in these basins up to the final stage — precipitation of the easily soluble salts [1]. The supply source determined not only the initial composition of the water in a basin but also subsequent evolution of the hydrochemical regimes and the superimposed metamorphization by solutions of different origin.

In isolated portions of the largest Permian potassium basins, potassium formations of chloridic and sulfate-chloridic type were sometimes formed simultaneously. The former were formations of intermediate salt basins open to the influx of water from a sea or the ocean. Sulfate-chloridic potassium formations of this kind are typical for terminal potassium subbasins. In the gigantic Kungur Cis-Ural halogenous basin — its Upper Pechora and Upper Kama subbasins — chloridic potassium formations were built up [10]. To the south, in the terminal Caspian subbasin [18], sulfate-chloridic formations developed. In the Dnieper-Donets depression, Asselian-Sakmarian potassium formations of the chloridic type appeared in the subbasin of the Bakhmut depression. To the northwest, a contemporaneous sulfate-chloridic potassium formation was deposited in the Poltava and Nezhin subbasins [16, 17].

All three types of potassium formation are known in the USSR. In detailed studies of potassium-bearing regions of the country, geologists have tried to determine which of these formations is more common for each of the three types. They adopted the Upper Kama formation as the standard of lithotypes of chloridic potassium formations; for sulfate-chloridic type, they took the near-Caspian formation; sulfatic formations were exemplified by the

potassium deposits of the Ciscarpathian region. New, geographic names were suggested for these three types of potassium formations to replace the geochemical terms. However, the names of Upper Kama, near-Caspian, and Ciscarpathian types of potassium formations as standard lithotypes never came to be generally accepted. This may be due to the fact that the potassium formations of these regions do not completely represent all the specific features of their counterparts in other regions. On the other hand, geochemical terms, besides their "seniority," clearly identify these formations.

Potassium formations of the chloridic type in the USSR include (besides Upper Kama and Upper Pechora), the Kungur formation, the Cambrian formation at the Nep deposit in Eastern Siberia, the Frasnian and Famennian deposits in the Pripyat depression, the Asselian-Sakmarian sediments in the Bakhmut depression, and the Upper Jurassic formation in Gaurdak. The common trait of all these formations is the fact that potassium salts are contained only in sylvinitic and carnallitic rock. As exceptions, potash deposits in some of these formations (e.g., Oligocene beds in the Upper Rhine graben) can consist almost entirely of sylvinites. The salt portion of formations of this type usually comprises a rock salt layer at the bottom overlain by a potassium zone, covered by a thinner layer of rock salt. At the base of such formations, beds and packets of anhydrites and carbonate rocks are frequent. Carbonate rocks usually form the base of these potassium formations, at least in the seaward portion of the basins.

However, chloridic potassium formations are not identical. While, most of these formations are saturated with salt, some have more clay and include layers and members of marlstone and clayey-carbonate rocks (such as the Famennian formation in the Pripyat depression). Potassium formations with a high concentration of salts that were formed in stable hydrochemical conditions with brine concentrations usually include a compact potassium zone. It appears as a group of near-lying potassium layers, with the lower ones made up of sylvinites and the upper one of carnallite. These formations have a directed common potassium accumulation cycle (halite $\rightarrow$ sylvite $\rightarrow$ carnallite). Other more "clayey" formations of this type contain several cycles in the potassium portion. It consists of numerous (10 or more) potassium layers, sometimes grouped in several horizons; each horizon consists mainly of sylvinite layers and often but not always is crowned by a carnallite rock. The direction of sedimentation in these potassium accumulation cycles is this: clay and carbonate (marlstone) $\rightarrow$ halite $\rightarrow$ sylvite $\rightarrow$ (sometimes) carnallite.

Chloridic potassium formations are typical for the Early Phanerozoic (Paleozoic), although some were periodically formed at later time (during the Triassic, Upper Jurassic, and Paleogene) [9, 15]. These are mainly formations of a marine origin, although ocean water flowing into semiisolated large halogenous basins also experienced significant metamorphization during prolonged migration. A contributing factor in this development was the fact that most potassium chloridic basins are associated with large, long, and narrow tectonic structures, such as piedmont troughs and grabens. As a result, by the time potassium-magnesium salts were precipitated, the brine in potassium basins was depleted of carbonate and sulfate ions.

The Upper Kama Kungur potassium formation [10] consists of three strata: a lower clayey-dolomite-anhydrite bed (average thickness 230 m),* a salt bed (400 m), and the upper salt-marl bed (100 m). The salt bed consists of (bottom to top): an underlying rock salt layer, a sylvinite horizon (7-40 m; average thickness 20-25 m), a sylvinite-carnallite horizon (average thickness 60-70 m), and the top salt cover [10]. In the sylvinite horizon, sylvinite layers are interstratified with rock salt layers. The lower three sylvinite layers consist of red sylvinite (average thickness 0.8-5.3 m); they are overlain by a striated sylvinite layer (average thickness 1.8 m).

The sylvinite-carnallite horizon comprises up to 10 carnallitic rock layers. In some locations (particularly in the bottom four layers) they are replaced by variegated sylvinite. Carnallite layers vary in thickness from 0.5 to 28 m, counting the bulges. The average thickness in locations where they consist of variegated sylvinite is 0.8-3.4 m.

The Upper Famennian Pripyat halogenous formation [2, 3] consists of two subformations: a lower halitic subformation (50-3250 m, average 559 m) and an upper potassium-bearing clayey-halitic subformation (50-2670 m, average ~1000 m). The halitic subformation typically includes pure rock salt members (up to 100 m), separated by thinner (up to 30 m) nonsalt rock members (anhydrite, carbonate, and terrigenous rocks). The average salt saturation of the subformation is 85-90%.

*Here and hereafter, numbers in parentheses indicate layer thicknesses.

The potassium subformation exhibits a frequent alternation of salt-containing and nonsalt members, varying in thickness from 30 to 50 m. The nonsalt rocks are usually carbonate-clay types (marlstone and halopelite). The rock salt is contaminated with impurities. The salt saturation of the potassium subformation is 25–75%. Depending on the completeness of sections, they may include from 2–4 to 60 potassium salt layers. The latter consist mainly of sylvinites and less carnallite-containing carnallitic rocks. The thickness of potassium layers ranges from 1 to 10 m (typically 2.5–5 m). The number of potassium layers is at most 20 in the individual sections of the potassium-bearing subformation. Only about 10 potassium layers of this subformation are of some commercial value.

The Upper Jurassic potassium formation of Central Asia [4, 22] consists of three beds: a lower carbonate-anhydrite bed, a salt bed, and a clayey-anhydrite bed. The carbonate-anhydrite bed in Gaurdak is associated with commercial authigenic sulfur deposits. In the Gaurdak-Kugitanga area, the salt section includes members of rock salt at the bottom (100–350 m), potassium-bearing members (300–500 m), and an overlying rock salt member (up to 50 m). The maximal thickness of the formation south of Kerki is 1400 m.

Two salt accumulation cycles have been identified in the section of the halogenous formation in the northern and eastern parts of the Amu Darya depression; in the Murgab-Bakharden zone there are three cycles. They begin with an anhydrite member (with limestone layers) and are crowned by thick salt members.

In the Gaurdak-Kugitanga region the potassium-bearing member contains potassium horizons. In the lower horizon, sylvinite lenses are superseded up the section by carnallite-sylvinite and then again by sylvinite. In the middle horizon the middle carnallite bed lies on a sylvinite bed (locally, with carnallite). The upper potassium horizon consists of sylvinite lenses and the upper carnallite bed. Potassium beds vary in thickness from a few meters to 23 m (average 3.1–9.5 m). The lower potassium horizons in the Karlyuk deposit are treated as one bottom layer. The total number of layers in the formation is 11. Sylvinites are also predominant over carnallites in this region.

The Cretaceous potassium formations of Brazil, Congo-Gabon, and Thailand-Laos represent a peculiar chloridic subtype. Besides sylvinite and carnallite rock layers, they contain beds of bischofite and tachyhydritic rocks. To some extent, this subtype is related to the potassium-bearing sulfate-chloridic formations that typically include bischofite rocks. Sulfate-chloridic potassium formations of the USSR include the Lower Permian halogenous beds in the Caspian syncline, the Dnieper-Donets depression, and the Baltic Zechstein syncline. Potassium — magnesium salts with a predominance of sylvinite and carnallite also include in these sections sulfuric acid salts — polyhalite, kieserite, kainite, and langbeinite — or rocks of a mixed mineral composition, such as hartsalz. Bischofite layers and boron-bearing salt rocks are also typical for this kind of potassium formation. Dolomites are prevalent amid intraformational carbonate beds; magnesite is also sometimes present.

Chloridic potassium—magnesium salts in potassium formations of the sulfate-chloridic type have a tendency to form succession up the section where sylvinites give way to carnallite and further to bischofite rocks. Polyhalite and kieserite are often associated paragenetically or stratiformally with sylvinites; carnallite rocks are associated with kieserite, kainite, and langbeinite. Hartsalz mixed-type rocks are characteristic of these horizons. Local anomalies are observed in the sections where the lower potassium beds consist of kieserite-carnallite rocks, while the upper potassium beds are sylvinitic. These anomalies could reflect metamorphization of brine or its migration (preparation) in a halogenous basin followed by diagenetic (in lower horizons) substitution of primary sedimentary potassium—magnesium salts.

It is a characteristic of the sulfate-chloridic potassium formations that the main evolutionary process with precipitation of chloridic potassium—magnesium salts was periodically combined with a superimposed sedimentation of sulfatic potassium—magnesium salts. With a higher sulfate content of the brine, precipitation of chloridic potassium salts could be preceded here only by sedimentation of sulfates — anhydrite and polyhalite.

Sulfate-chloridic potassium formations were generally accumulated during the Permian. Their sections reflect not only the general evolutionary trends of potassium—magnesium salt sedimentation but also certain features (differences) of their lithology and especially different intensities of accumulation of sulfatic potassium — magnesium salts, bischofite, and borates.

In the section of the Kungur potassium formation in the Caspian syncline [5, 7, 18], 10 rhythms, or salt accumulation cycles, are distinguished. At the base are dolomite-anhydrite or anhydrite beds, followed by thick rock salt members that include potassium and magnesium salt layers. In rhythms 2–5, potassium — magnesium salts are represented mainly by polyhalite and polyhalitic rock layers. These layers are the thickest in the Aktyubinsk Cis-Ural region. At the top of this lower half of the section, sylvinite and kieserite are present besides polyhalite. Up the section, potassium — magnesium layers in four rhythms are composed of sylvinite and carnallitic and bischofite rocks.

Polyhalite, kieserite, and sometimes kainite are often associated with sylvinite deposits. Carnallite rocks exhibit diverse mineral compositions and often include substantial quantities of kieserite, sylvite, or bischofite. These beds are often accompanied by accumulations (nests or lenses) of langbeinite rocks. Carnallitic rocks of the Caspian region are rich in bromine and rubidium.

In the past, the five lower rhythms of the Kungur halogenous formation of the Caspian syncline were classified as part of the underlying rock salt layer; the upper, tenth member was treated as an element of the covering rock salt. Only the remaining four members were identified as the potassium-bearing zone. Indeed, these four rhythms in the section contain the region's commercially important beds of chloridic potassium — magnesium salts.

The thickness of the Kungur potassium formation in the Caspian syncline attains 1.2 km in its marginal parts, inside the syncline it increases to 3 km. The visible thickness grows to 10 km in the arches of salt dome structures due to salt tectonics. At the center of the syncline the salt saturation of this formation attains 80%.

On the area of the Caspian region the potassium formation is represented in the margin by salt-free (terrigenous, carbonate, and sulfate) lithologic complexes; inside the syncline, it consists of internal salt lithologic complexes [12]; from the perimeter to the center of the syncline the halitic lithocomplex gives way to polyhalitic-halitic rocks (represented by locally thenardite-halitic rocks in the southwest), then to sylvinite-halitic, carnallite-sylvinite-halitic, and finally, in the north central and northwestern parts of the syncline to a bischofite-carnallite-sylvinite-halitic complex. The distribution of complexes reflects the evolution in the sedimentation of potassium — magnesium salts and the reduction of the time of accumulation of the potassium basin (with displacement of the intensive subsidence area).

The Lower Permian potassium formation in the Dnieper-Donets depression [16, 17] consists of a lower potassium-free part (asselian) and an upper potassium-bearing part (Sakmarian). The potassium-free part of the formation (up to 1000 m thick) consists of argillite, carbonate rock, anhydrite, and rock salt members. Seven salt accumulation cycles are distinguished; salt saturation grows in the upper part of the section. In the potassium-bearing part of this formation (the Kramatorsk suite), up to 700 m thick, an additional three salt accumulation cycles are distinguished [8-10]. Each of these is associated with a bed or a group of near-lying beds of potassium salt. The lowest of these cycles (cycle 8) includes a bottom kieserite-carnallite bed which locally contains kainite and bischofite rock interlayers. The cycle also includes a higher-lying sylvinite layer. In the peripheral parts of depressions the stratigraphic analogues of these two layers consist of a polyhalitic rock. The ninth cycle includes an additional two sylvinite layers, which make up (together with the lower sylvinite layer) the middle sylvinite zone in the Kramatorsk suite section. Finally, a sylvinite-carnallite horizon is contained in the uppermost (tenth) cycle. In the Mashevsk section it is made up of five 2-4 m interlayers. The lower interlayers consist of carnallitic rock; the upper ones, of sylvinite. At Svyatogorsk this horizon is represented by sylvite-kieserite-langbeinite hartsalz.

The potassium salt saturation of the Kramatorsk suite normally ranges from 4 to 6%, sometimes rising to 12%. The lower and upper beds contain borates (colemanite, ascharite, and sulfoborite) in kieserite-carnallite rock, which is characteristic of potassium formations of the sulfate-chloridic type. High bromine content (up to 0.53%) has been established in the bischofite rock.

In the section of the Zechstein potassium formation that stretches from Britain through the Netherlands, Denmark, West Germany, East Germany, and Poland to the Soviet Baltic, six salt accumulation cycles are now identified. Four of these cycles (series) contain potassium salts (Werra, Stassfurt, Leine, and Aller). The uppermost cycles of the formation are thin and of limited practical importance. The thickest units are the lower three series: Werra (up to 375 m), Stassfurt (up to 600 m), and Leine (up to 350 m). In the Soviet Baltics only the lowermost layers of the Werra series contain potassium salt.

The Werra series in East and West Germany is represented by the following horizons (bottom to top): basal conglomerate (up to 2 m), cupriferous shale (up to 1 m), limestone (6-8 m), anhydrite (6-8 m), rock salt (350 m), and the Thuringen (2-10 m) and Hessen (2-15 m) potassium interlayers. Anhydrites form localized anhydrite bars; the rock salt thickness is reduced equivalently above the elevated portions of these bars. In the centralmost subsided portions of local depressions, potassium beds consist mainly of carnallite and kieserite-carnallite rocks. Toward the perimeter of depressions and above elevations, the beds grow thinner and become of a hartsalz type, with kainite and polyhalite being quite common, besides kieserite and sylvite.

In the Baltic syncline [21], the Werra series section contains one potassium horizon up to 37 m thick. In Poland, west of the Gulf of Gdansk, it includes interlayers and layers of polyhalitic and anhydrite-polyhalitic rock. In the Kaliningrad region this horizon begins with polyhalite interlayers, succeeded up the section by interlayers and

bed of kieserite-halite and kieserite-polyhalite rocks, overlain by sylvite-kieserite hartsalz and kainite rocks. The polyhalitic facies is typical for peripheral parts of subbasins or elevations sometimes surrounded by anhydrite bars.

In the Stassfurt series the potassium bed at the center of Western Europe also consists mainly of a carnallitic rock and, partly, hartsalz. Locally, it contains sylvite-kieserite, kainite, and langbeinite rocks, and also polyhalite, glauberite, loewite, and tachyhydrite interlayers with boracite (stassfurtite) nodules. The potassium layer varies in thickness from 5-10 to 30-40 m.

The Leine series includes the Ronnenberg potassium bed (10-25 m) and the Riedel bed (6-10 m), and locally the Bergmansegen (0.5-2.0 m) and Albert (2-6 m) potassium beds. They consist mainly of sylvinites, but sometimes also of kieserite-carnallitic rock and hartsalz. The presence of boracite in sylvinites and carnallite veinlets in above-lying marls may indicate that sylvinites were formed by substitution of carnallite rock. Near Groningen (the Netherlands) the Ronnenberg bed consists of a carnallite rock.

In the Aller series (over 100 m) in the North German and Weser depressions, a bed of 3-5 m low-concentration kieserite-sylvinites is found locally.

Sulfatic potassium formations are almost unique. Conditions favoring their development existed only during the Miocene in potassium-bearing sediment of the Ciscarpathian trough and the Central Sicilian depression. In both regions, potassium formations are underlain by clays and marls; in the Carpathian region these formations consist mainly of salt-bearing sand-clay sediments with single thin anhydrite layers. In Sicily the subsalt portion of the section of this formation consists of Cattolica gypsum, overlain by marl-anhydrite breccia. In both regions, potassium formations accumulated in elongate basins with various degrees of sagging of the transverse blocks.

In the Ciscarpathian trough [19] three suites contain potassium salt: the Lower and Upper Vorotyshchen and the Upper Stebnik. Salinized argillites and sandstones are predominant in these sections. They are brecciated to different degrees. The section also contains beds and members of a clayey, sometimes more homogeneous, halitic rock, and potassium — magnesium salt beds. The degree of salinization of the rocks of potassium formation sections varies widely. The Lower Vorotyshchen potassium formation is 500-900 m thick; the Upper Vorotyshchen potassium formation is up to 600-1000 m thick; the Upper Stebnik formation is up to 300-600 m thick.

In each of the above-mentioned potassium formations, the bulk of potassium salt is found at two to five levels. Usually, with increasing formation thickness (in the tectonic blocks subducted more deeply), the sections become saturated with salts and potassium, and the number of potassium — magnesium salt layers increases, as does their thickness. These deposits are of a stratal or lenslike shape.

Potassium — magnesium salt deposits have been found at two to four shelves in the sections of the Lower and Upper Vorotyshchen formation. They are less than 100 m thick; in the Upper Vorotyshchen, they are sometimes 60 m thick, and up to 100 m in "swollen" areas. In both these formations the beds consist of langbeinite-kainite and langbeinite rocks, as well as rocks of a more complex mineral composition, such as hartsalz, which also includes sylvite, kieserite, polyhalite, schoenite, carnallite, epsomite, astrachanite, leonite, loewite, vanthoffite, etc. Polyhalite rock interlayers are sometimes found at the base and in the roof of the beds of these mainly sulfuric acid — potassium — magnesium salts. In some of the salt-saturated sections of these formations, which include thick clayey rock salt members but no substantial potassium beds, potassium salts may be found only as insets, interlayers, or thin layers of polyhalitic rock.

Salt-bearing sand-clay rocks, to some extent brecciated, are also common in the section of the Upper Stebnik potassium formation that stretches from Hodnoviczi through Morsha and Kalusz to Jablonow. At the bottom of the section thin anhydrite beds and in the middle parts clayey rock salt beds are sometimes found. At two or three levels, lenslike kainite and langbeinite-kainite rock beds are present; the latter include a noticeable kieserite, sylvite, and polyhalite admixture. In the Kalusz-Golyn deposit, stratal lenses of layered sylvinites are present at two levels. The thickness of sylvinite deposits is at most 12 m; the sulfuric acid — potassium — magnesium salt layers are usually 20-30 m thick, up to 45-50 m in swollen portions.

The concentrations of secondary components (bromine, boron, and rubidium) in potassium — magnesium salts are usually low in the Ciscarpathian potassium formations because of their high clay content. At the base of the Lower Vorotyshchen potassium formation, where the anhydrite member is found, a minor sulfur presence has been registered. In the interformational terrigenous Zagorsk member, which separates the two Vorotyshchen potassium formations at Truskavets and Dzvinych, polymetallic mineralization (galena and brunnite) has been described.

In the Upper Miocene potassium formation at Messina (Sicily), up to 1400 m thick, underlain and overlain by marlstones, the middle portion of the section consists of a salt bed. The lower and upper portions are comprised of gypsum-bearing rocks. The lower part of the salt bed consists of rock salt with gypsum and clay.

At the upper part of the salt bed a potassium-bearing zone (up to 100 m) is present. It begins with a polyhalite-halite subzone at the bottom represented by rock salt with polyhalite interlayers. Up the section it is succeeded by a kainite subzone (up to 50 m) with astrachanite at the top; it is followed by a carnallitic (5-10 m) subzone with lenses of carnallitic rock and locally sylvinites, sometimes also bischofite. The potassium zone section ends in a kieserite subzone (up to 15 m) at the top. Stratal lenses of kainitic rock are 1.5-8.0 km long and 0.6-3.0 km wide. Five commercial kainite beds, from 2 to 20 m thick, are found in the kainite subzone between Caltanissetta and Enna.

Commercial sulfur deposits are associated with peripheral gypsum-carbonate complexes (up to 100 m) of the potassium formation of Sicily in the Trapani-Licata-Etna triangle.

The typology of potassium formations according to the mineral composition of commercial potassium — magnesium salt deposits determines the specific salt sets in various formation types. This distinct specialization provides a benchmark for forecasts. There are direct correlations between higher contents of certain trace components, such as bromine in sylvinites, carnallite, and bischofite rocks and rubidium and cesium in carnallite rocks. These components can be extracted simultaneously from potassium — magnesium salts of chloridic and sulfate-chloridic potassium formations. The higher boron content is typical for sulfate-chloridic potassium formations; residual borate deposits are associated with their hypergenic units. Most potassium formations that contain contacting carbonate and gypsum-anhydrite beds also contain a certain amount of authigenic sulfur. Sulfur formation was especially intense in peripheral lithologic complexes of these strata or in caprocks of salt domes, where sulfate reduction was more vigorous.

Finally, some of the interformational carbonate horizons of potassium formations include signs of celestite, fluorite, and lead-zinc mineralization. Metallization of cupriferous sandstones and shales is associated with terrigenous horizons of strata that contain potassium formations [13, 14]. This is particularly true of regions of Permian potassium formations. The lithotype of potassium formations thus presents a distinct specialization of a vast set of minerals.

LITERATURE CITED

1. M. G. Valyashko, *Geochemical Patterns in the Development of Potash Salt Deposits* [in Russian], Izd. Mosk. Gos. Univ., Moscow (1962).
2. R. G. Garetskii, É. A. Vysotskii, and V. Z. Kislik, *Potash Salts of the Pripyat Trough* [in Russian], Nauka i Tekhnika, Minsk (1984).
3. R. G. Garetskii, É. A. Vysotskii, and V. Z. Kislik, *Potash-Bearing Basins of the World* [in Russian], Nauka i Tekhnika, Minsk (1988).
4. V. V. Gerasimova and V. I. Sedletskii, *Potash Salts of Southern Central Asia* [in Russian], Izd. Rost. Univ., Rostov-on-Don (1969).
5. V. S. Derevyagin, S. A. Svidzinskii, V. I. Sedletskii, et al., *Lower Permian Halogenous Formation of the Northern Caspian Region* [in Russian], Izd. Rost. Gos. Univ., Rostov-on-Don (1981).
6. N. M. Dzhinoridze, S. D. Gemp, A. F. Gorbov, et al., *Distribution and Exploration Criteria of Potash Salts in the USSR* [in Russian], Metsniereba, Tbilisi (1980).
7. M. D. Diarov, "Potassium prospects of halogenous formations of the Caspian depression," *Tr. KazNIGRI*, Issue 6 (1974).
8. M. A. Zharkov, *Paleozoic Salt-Bearing Formations of the World* [in Russian], Nedra, Moscow (1974).
9. M. A. Zharkov, "Classification of salt-bearing formations and the evolution of salt accumulation during the Phanerozoic," in: *Evolution of Lithogenesis in the Earth's History* [in Russian], Nauka, Novosibirsk (1981), pp. 4-12.
10. A. A. Ivanov, *Permian Salt-Bearing Basins of the Pechora-Kama Cis-Ural Region* [in Russian], Nauka, Novosibirsk (1965).
11. A. A. Ivanov and M. L. Voronova, *Halogenous Formations* [in Russian], Nedra, Moscow (1972).

12. S. M. Korenevskii, "Distribution of lithofacies complexes of halogenous formations," in: *The Present State and Objectives of Soviet Lithology*, Vol. 3 [in Russian], Nauka, Moscow (1970), pp. 32-39.
13. S. M. Korenevskii, *The Set of Minerals of Halogenous Formations* [in Russian], Nedra, Moscow (1973).
14. S. M. Korenevskii, "Halogenous Formations of the Russian Platform: Typology, distribution patterns, and accessory minerals," in: *Basic Problems of Salt Accumulation* [in Russian], Nauka, Novosibirsk (1981), pp. 122-131.
15. S. M. Korenevskii, "Evolution of potassium basins and potassium formation types during the Phanerozoic," in: *Evolution of Sedimentary Processes on Continents and Oceans (Proceedings of the 12th National Lithologic Conference)* [in Russian], Nauka, Novosibirsk (1981), pp. 225-227.
16. S. M. Korenevskii, V. P. Bobrov, K. S. Supronyuk, et al., *Halogenous Formations of the Northeastern Donets Basin and the Dnieper-Donets Depression and Their Potassium Prospects* [in Russian], Nedra, Moscow (1968).
17. S. M. Korenevskii, G. I. Vakarchuk, V. M. Zakharova, et al., "Correlation of sections, potassium prospects, and lithofacies complexes of the Kramatorsk suite of the Dnieper-Donets depression," *Geol. Zhurn.*, 40, 48-56 (1980).
18. S. M. Korenevskii and M. L. Voronova, *Geology and Formation Conditions of Potassium Deposit in the Caspian Syncline in the Southern Part of the Cis-Ural Trough* [in Russian], Nedra, Moscow (1966).
19. S. M. Korenevskii, V. M. Zakharova, and V. A. Shamakhov, "Miocene halogenous formations of Carpathian peidmont," *Tr. VSEGEI, Nov. Ser.*, 27, (1977).
20. S. M. Korenevskii and Yu. V. Poborskii, "Zechstein halogenous formation in the subsidiary Gdansk-Kaliningrad basin and its potassium prospects," in: *Structure and Formation Conditions of Potash Salt Deposits* [in Russian], Nauka, Novosibirsk (1981), pp. 161-171.
21. S. M. Korenevskii, A. L. Protopopov, and A. A. Shaporev, "Kainite rock placers in the zechstein of the Baltic region," *Litol. Polezn. Iskop.*, No. 1, 71-80 (1983).
22. V. M. Popov, *Potassium and Sulfur Prospects of the Upper Jurassic Halogenous Formation in Central Asia* [in Russian], Fan, Tashkent (1988).
23. V. I. Raevskii, M. P. Fiveg, V. V. Gerasimova, et al., *Deposits of Potash Salts in the USSR: Exploration and Prospecting Methods* [in Russian], Nauka, Leningrad (1973).

OCCURRENCE FORMS AND DISTRIBUTION BALANCE OF INDICATOR ELEMENTS IN TIN-BEARING PLACERS

N. G. Patyk-Kara, L. P. Dolgoplova, and L. I. Serdobova

UDC 550.4:553.451

The geochemical aspects of concentration and dispersion of ore material in the formation of placer deposits are studied. The distribution of the main chemical elements associated with tin in the metallization process and occurring in geochemical anomalies formed in connection with placers is described; the analysis is based on a determination of grain size classes of the primary tin deposits, an investigation of the monomineral fractions of heavy and light mineral, and chemical extractions. The forms of occurrence of these elements in tin sediments are described; a theory is presented for the formation of ore anomalies above buried placers in the littoral shelf zone. Distribution balances of tin, copper, zinc, lead, and silver are calculated as major elements of metallogenic anomalies associated with tin placers.

The geochemical aspects of concentration and dissemination of ore matter in the formation of placer deposits have been increasingly studied in recent years. According to the authors of [14, 15, 20], placers cannot be interpreted as a product of mechanical separation of clastic material. It is essential to take into account the geochemical evolution of placer-carrying sediments. This approach largely rests on data derived from experimental, methodological, and exploratory works which demonstrated contrast of placers in geochemical fields [3, 7, 11, 13, 21]. It was proposed that geochemical prospecting is an efficient method for finding and appraising deposits, especially buried placers in the littoral zone, where alternative methods for collecting direct data on ore mineral accumulations are unavailable [6].

Geochemically, a placer is a variety of mechanical flows and dispersion haloes. In turn, as ore accumulations, placers give rise to primary (syngenetic) and secondary dispersion haloes. According to Polykarpochkin [8], the mechanisms of differentiation and transport of material in these haloes is diversified. Clastogenic ore material in placers can be transported — depending on the main denudation agent — either by diffusion in the bulk of clastic matter, or by gravity, or by transport of particles via another moving medium (mainly water). Besides mechanical transport, true solutions or a colloid phase have an important role. They are carried by lateral or vertical migration streams. Vertical flows are especially important since they form above-placer haloes over buried placers brought out of an active deposit formation sphere. These processes may have different types of kinetics. In particular, the rise of matter in haloes of ascending migration seems to be mainly controlled by diffusion in water and gas media and capillary rise of solutions. It can also occur under the effect of pressurized water. Ionic exchange, electrochemical phenomena, and osmosis at the interface of different media (in particular, at the front of freezing and thawing in permafrost rocks) can play an important role [14].

These general principles need checking in the case of haloes of each particular deposit, formed or altered in various lithogenetic settings, especially considering that available information indicates ambiguities in the behavior of various elements in placer haloes, which complicates interpretation of geochemical data.

A detailed sounding of metalliferous sediments has been performed in the contour of a tin placer situated in the littoral-shelf zone of an eastern Arctic basin. The objective was to study the geochemical anomalies associated with placer deposits, the forms of occurrence of metals in their haloes, and the balance of their distribution in various grain size and sediment classes.

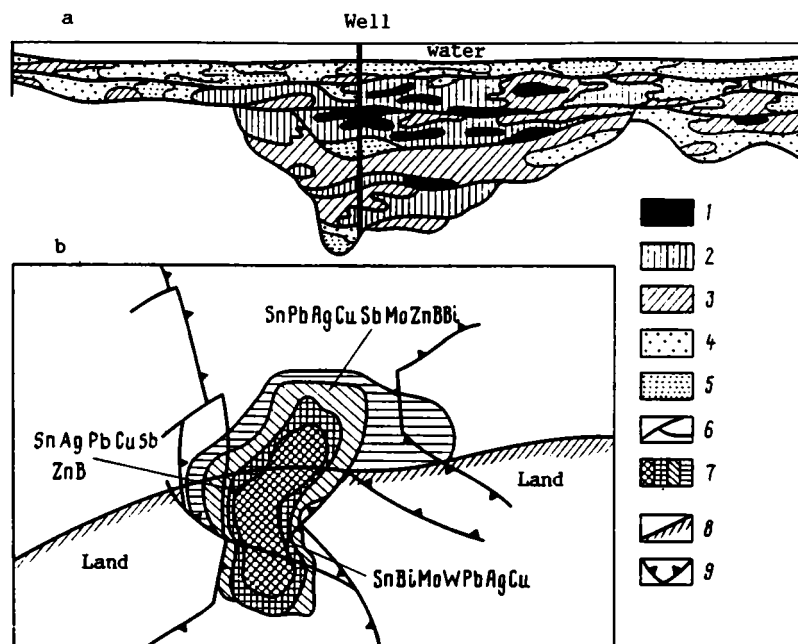


Fig. 1. Geochemical section of tin placers in the littoral-shelf zone, area of collection of reference geochemical and balance samples (a) and its representation in surface sediments (b): 1-4) complex geochemical anomalies and their composition (1 — highly contrastive, type $\text{Sn}_{120}\text{Cu}_{10}\text{B}_{5-7.5}\text{PbAg}_{4-5}\text{W}_4\text{Bi}_2$; 2 — contrastive, type $\text{Sn}_{50}\text{Cu}_{13}\text{PbAg}_8\text{B}_6\text{W}_4\text{Bi}_2$; 3 — moderate, type $\text{Sn}_{15}\text{Cu}_{10}\text{Pb}_7\text{Ag}_5\text{B}_4\text{Zn}_3\text{W}_2$; 4 — weak, type $\text{Cu}_8\text{Sn}_7\text{PbAg}_3$; 5) geochemical background; 6) boundaries of beds; 7) complex geochemical anomaly above the placer and its contrastivity (a — very high, b — high, c — medium, d — weak); 8) coastline; 9) faults bounding the buried graben valley. Chemical symbols specify the composition of the anomaly in its various zones. The section represents the borehole where balance samples were collected.

The placer is situated in a buried graben-valley of a submeridional course. It is a complex polygenetic entity. Its lower horizons occur on the weathering crust of a Late Cretaceous-Eocene (?) age and of continental genesis. This part of the placer was formed during fluvial cycles, encompassing the Miocene-Lower Pleistocene. In the southern part of the deposit and on the sides of the graben-valley, older alluvial pebblestones, apparently of an Eocene-Oligocene age, have been preserved. The upper portion of the placer on that part of the deposit is of a littoral-marine genesis and includes the placer's richest bed apparently of a Lower to Middle Pleistocene age. The top of the section consists of littoral-marine sediments formed during the Upper Pleistocene (Kargi) and Holocene (postglacial) transgressions.

The section of the placer displays a trend toward gradual transformation of terrigenous material as a result of erosion and redeposition of the products from the crust of weathering. Toward the top, the sediment becomes better sorted; there is a relative accumulation of material of silt size and a loss of clay matter. Clay minerals in all specimens consist of more than 50% kaolinite, with hydromica and chlorite admixtures. The highest proportion of kaolinite (~80%) in the pelitic part of the sediment is typical for ancient alluvium: it is higher by almost a factor of two than in the underlying crust of weathering, indicating erosion of the profile's top at that time. In the Pleistocene part of the section, kaolinite content declines (to 60%), accompanied by a gradual rise of the share of hydromica (25%) and especially chlorite (~12%). We will demonstrate that these differences in the mineral composition of the pelitic component of the sediment are manifested in different efficacies of sorption of various elements found in the halo of tin placers. Different degrees of sorting of the material are also reflected in the distribution of elements associated with accessory and ore minerals that accumulate in the heavy fraction of the sediment.

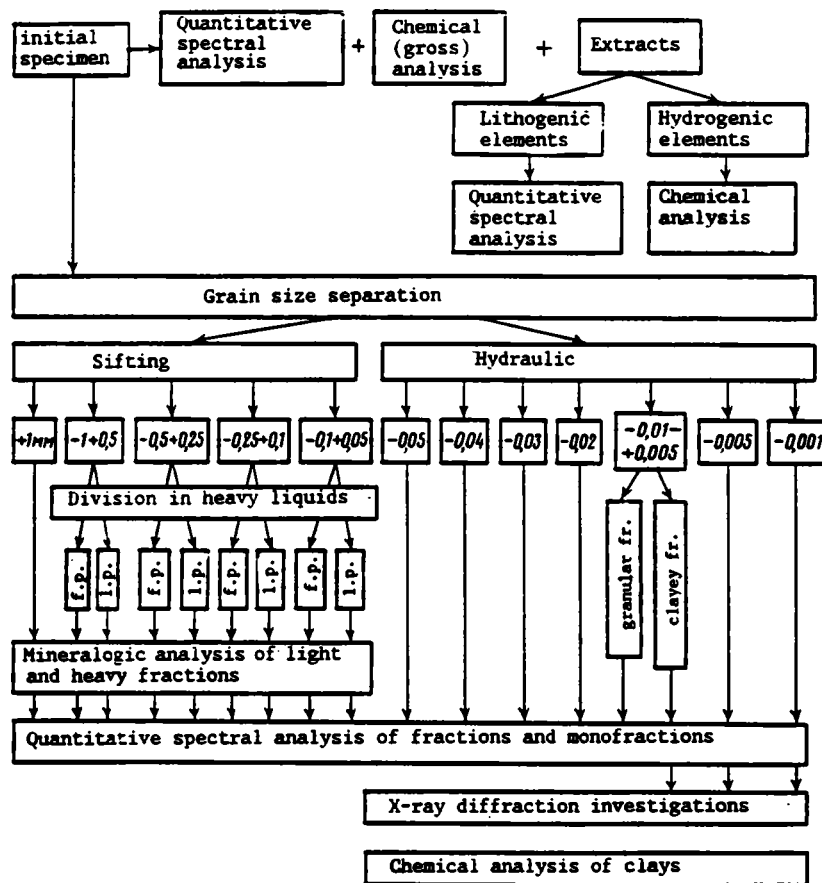


Fig. 2. Processing and analysis of geochemistry specimens of the reference section in detailed lithologic-geochemical investigations

The entire tin deposit section has substantially higher concentrations of elements that are concomitant with tin in the metallization process, primarily elements of the chalcophilic group: boron, tungsten, etc. [3, 6, 17]. The concentration levels vary considerably in the section from the richest parts of metalliferous placers to the halo as a whole, including the above-placer halo and the Upper Pleistocene and Holocene littoral-marine sediments under which the placer is buried. A generalized geochemical section of the placer constructed by the TLOG program (written by L. N. Ginzburg, Institute of Mineralogy, Geochemistry, and Crystallochemistry of Rare Elements) for this locality is presented in Fig. 1a.

An important distinctive feature of the halo space of the placer is the fact that, in recent floor sediments in the shelf, it appears as a contrastive complex geochemical anomaly of this form: $[Sn_{16}PbAgCu_3SbNoZnB_2][Ba_3ZrNbYb_2YTiLa_{1,5}]$ (see Fig. 1b). Besides the indicator elements of the metallogenic process itself, which reflects in a modified form the specialization of the root source of the placer (the first part of the formula), it also includes a group of elements indicating natural sliming on the first mechanical barrier (the second part of the formula) [7]. The low concentration coefficients (KK) of Ti, Zr, Nb, and Y, on the other hand, show that the process was suppressed, which matches the theory of the recent lithodynamics of this part of the coastal zone.

Method of Study. The distribution of indicator elements according to grain size classes and mineral fractions were studied on a series of reference samples collected in the section of the placer with consideration for the lithologic variability and genesis of sediments. The small-grained component of the sediment was first sifted to isolate the class of not less than 1 mm that is typically investigated in the general studies of haloes of placer deposits. It was then subjected to detailed fractionation (into 14 classes) and studied according to the scheme of Fig. 2. We also investigated the concentration of impurity elements in monomineral fractions, especially in the dominant rock-forming minerals of

the granular component (quartz and feldspar), clay matters, certain minerals of the heavy fraction (cassiterite, tourmaline, epidote, ilmenite, etc.), and diagenetic minerals (siderite and pyrite).

All chemical analyses were conducted by atomic-emission spectral investigations according to the method developed by the Institute of Rare Elements. Acetate extracts and Chester's extracts were prepared to study mobile metal forms. The low concentrations (hundredths and thousandths of a percentage point) of trace elements in most classes and fractions made application of direct methods (such as microprobe) impossible. However, the stability of the analytic results, their reproducibility on control specimens, and the similarities of balances calculated by different procedures convinced us that the final results are reliable. Classes and fractions were defined as concentrators of indicator elements in placer haloes, and conclusions were drawn concerning possible forms of their occurrence in metalliferous sediments. These data were used as the basis for studying the balance of major metallogenic elements according to the main technological sediment classes and their mineral components.

For this purpose, a combined balance sample was formed from the partial specimens of productive deposits in Lower and Middle Pleistocene littoral-marine placers in the depth interval of 8-14 m. The scheme of study of this composite specimen is illustrated by data compiled in Tables 1 and 2.

Elements found in higher concentrations were divided into three groups for the tin deposits based on the distribution in psammitic, siltic, and pelitic sediment components. The concentration of elements of the first group — Sn, Zr, Y, Yb, Nb, and B — grew steadily from the pelitic to siltic fraction and partly to the small-psammitic fraction, then dropped sharply in the larger-sized sand material (Fig. 3a). The second group are elements with concentrations increasing steadily from the silt to subcolloid fraction, either gradually — Ga, Cr, and V (see Fig. 3b) — or steeply — Al, Cu, Sc, Be, Zn, Pb, and Ni. The relative accumulation of Cu, Sc, and Be is pronounced in the subcolloid fraction (see Fig. 3c). By way of convention, the elements with unstable distributions of concentrations among grain size classes in these sediments were combined in the third group: Ag, W, Ba, Bi, Fe, and Mn.

We will describe the details of the behavior of typical elements.

The distribution of hydrolysate elements is not unequivocal. Aluminum reflects the distribution of two mineral groups on the chart — feldspars and clays. This accounts for the stable level of aluminum concentrations in grain classes and a noticeable maximum in pelitic material associated with kaolinite and hydromicas, especially the former. A slight Al maximum in the 0.01-0.05 mm classes can be attributed to the presence of high-alumina minerals, as determined by mineralogic investigations — andalusite, disthene, and sillimanite (see Fig. 3c). Gallium displays a similar regularity. It can substitute Al isovalently in clay minerals and feldspars. Some differences in its behavior in the pelitic part of the grain size spectrum apparently reflect the fact that Ga in clays is more closely associated with hydromicas than with kaolinite. A higher concentration of carbonic matter in this horizon also is a contributing factor: it is known to be conducive to gallium concentration [4, 10, 12]. The distributions of lithium and beryllium are similar the distribution of aluminum in pelitic material. This may be due to the possibility of heterovalent substitution of Al in clay minerals by these metals. On the other hand, Be concentration in coalified vegetable organic matter is higher by a factor of 2-5 than in clay matter.

Hydrolysate elements associated with clastogenic minerals (made up mainly of the heavy fraction) exhibit a different behavior. These are titanium (with some of its features discussed later), zirconium, yttrium, ytterbium, and niobium. Titanium is a distinct clastophilic element. Its concentration in these sediments is mainly associated with accessory ore minerals: ilmenite, leucoxene, rutile, and, to a lesser extent, sphene. Besides, higher Ti contents (0.5%) have been observed in sideritic nodules. In sediments with different degrees of sorting there is a clear correlation between Ti distribution in the grain size spectrum and the proportion of clastogenic minerals of the heavy fraction. Thus, in littoral-marine sediments the maximum of titanium is associated with coarse (0.5-0.1 mm) silt. According to mineralogic analysis, this reflects the predominant concentration of clastogenic accessory titanium minerals in that grain size class.

The second peak of Ti distribution is typical for fine (≤ 0.02 mm) silt. Anticipating, we will note that this class generally has the highest concentration of hydrolysate elements among all the specimens studied, including Zr, Y, Yb, and Nb. In psammitic material, Ti content does not exceed 0.01-0.02%, which is consistent with the grain size distribution of heavy minerals. Minerals of the light fraction are also Ti carriers. The constant Ti concentration in monofractions of feldspar and quartz throughout the grain size spectrum suggest isovalent substitution of Al and Si by Ti in these minerals.

A relative increase of Ti concentration is also observed in pelitic material, especially in specimens with a high kaolinite content. This suggests the possibility of Ti presence in colloid-dispersed compounds.

TABLE 1. Tin Balance (I)

Grain size class, mm	Yield of class, %	Mineral or physical composition of fractions	Mineral content of fraction, %	Element content in mineral, g/ton	Distribution of element in class, %	Average element content in class, g/ton	Distribution of element in specimen, %
-2,0 + 1,0	6,42	Rock fragments	25,00	30,00	45,87	16,35	0,14
		Quartz + feldspar	75,00	11,8	54,13		0,17
-1,0 + 0,05	52,02	Кварц + полевые ш	93,73	11,8	2,0	553,18	1,72
		Rock fragments	3,85	21,0	0,15		0,13
		Cassiterite	0,05	788000*	71,22		61,26
		Epidote	0,37	30,0	0,02		0,02
		Tourmaline	0,515	33,0	0,03		0,03
		Siderite	0,13	-	-		-
		Pyrite	0,34	10,5	0,006		0,01
		Ilmenite	0,34	30000 †	18,44		15,86
		Leucoxene	0,15	30000 †	8,13		7,00
		Anatase	0,10	Not analyzed			
		Rutile, sphene	0,006	"			
-0,05 + 0,01	10,55	Quartz + feldspar (admixture of accessories)	100,0	240,0	100,00	240,00	757
-0,01 + 0,005	10,90	Quartz + feldspar	80,42	100,00	86,52	92,95	2,62
		Clayey matter	19,58	64,0	13,48		0,41
-0,005	20,11	Clayey matter	97,51	51,0	97,18	51,17	3,0
		Coaly matter	2,49	58,0	2,82		0,09

*From published data.

†From laser spectral analysis.

TABLE 2. Tin Balance (II)

Characteristics of material	Fraction content of rock, %	Element content, g/ton	Distribution of element in mineral fractions, %
Initial specimen (gross)	100,00	310,0	100
Specimen constitution:			
Rock fragments	3,6	25,0	0,29
Quartz + feldspar	72,90	11,8	2,77
Clayey matter	22,24	50,0	3,59
Coaly matter	0,50	58,0	0,09
Heavy fraction minerals (class + 0.05 mm)	See balance (I)		90,84
Allothigenic	-	-	(90,83)
Authigenic	-	-	(0,01)

In this context, the second titanium maximum in floor sediments of the littoral-shelf zone of Arctic seas may be of interest. It is not related to the first mechanical barrier, where the relative accumulation of the heavy fraction takes place, including titanium minerals. The "second titanium maximum," first discovered by us in semiisolated bays and estuaries of the eastern Arctic coast [7], usually occurs outside the active wave zone and is typically confined to submerged deeps and flooded valleys. In these settings, titanium forms linear anomalies, often in combination with Mn and V, with stable correlations (0.75 and 0.65, respectively). Cr is often also found in these anomalies.

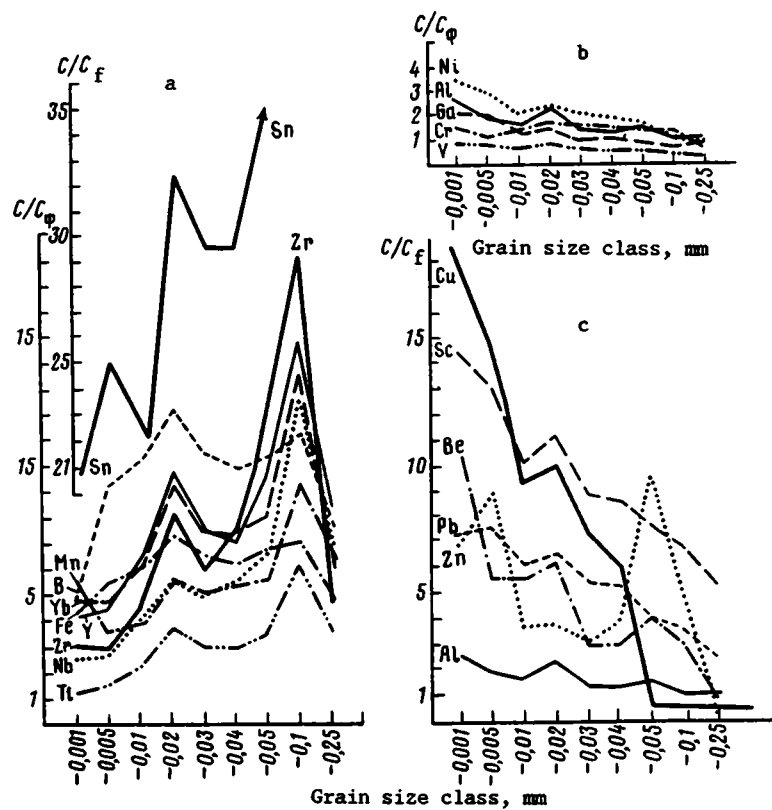


Fig. 3. Main distribution types of chemical elements in grain size spectrum of tin sediments (C/C_f = element concentrations valuated by background level).

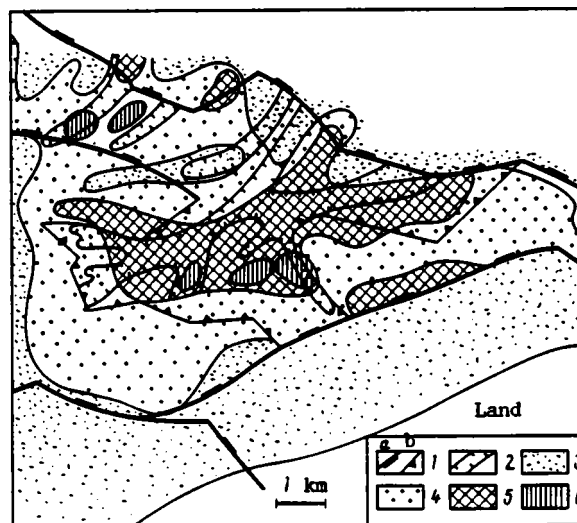


Fig. 4. Comprehensive anomaly of zinc, silver, and molybdenum in recent active layer of seafloor sediments over buried placer: 1) faults limiting the steps of bedrock layer (a) and buried graben valley (b); 2) buried valleys. Values of multiplicative indicator $Ag \times Mo \times Zn$: 3) background; 4-6) above background (4 - by a factor of 1.5, 5 - by a factor of 2-9, 6 - by a factor of 10 and more).

Titanium anomalies in all these situations coincide spatially with locations of relative accumulation of finely dispersed coalified vegetable organic matter (in the form of detritus). This suggests that the "second titanium maximum" is of a sorptive nature. The local geochemical barriers described by Migdasov [5] are likely to develop in these conditions and violate the correlations between titanium and aluminum and other hydrolysate elements. At any rate, in these environments Ti is a less reliable indicator for identifying placer areas than, for example, Zr, Nb, Y, or Yb.

Anomalies of this type have been observed in bays with suppressed lithodynamic processes. The anomalies are oriented at an angle (relative to the recent lithodynamic zone). Yet, they are in conformity with the plan of buried valleys, which prompted us to the hypothesis of their genetic relationship to these forms of seafloor and buried relief [6].

There is also a good correlation between Mn and Ti in the granular part of the specimens. It is attributed to isomorphic inclusion of Mn in main titanium minerals, according to spectral laser investigations performed by Kosovts (Institute of Rare Elements), who found that its concentration in ilmenite is above 10%, and in leucoxene, 0.3%.

Manganese and titanium reveal the complex nature of the anomalies controlled by different forms of their occurrence in placers. Mn is linked in a dual way with the clay minerals of the dispersed sediment component: partially by being an element of chlorite where it can be an isomorphic substitute for Fe and Mg, and partially in a dispersed hydrogenic form, as is often observed in zones of mixing of estuarine and bay waters. Likewise, the granular part of the specimens includes, besides Mn, its hydrogenic form in primary (in this case, ore) minerals: it is present in siderite nodules concentrated in coarse-silt and psammitic (0.1-0.25 mm) classes, which are also concentrators of V, Mo, Co, and other elements. Some of the Mn, V, Co, and Mo may be associated with coalified organic matter spread throughout the grain size spectrum [2, 4, 18].

We have mentioned that the clastogenic nature of anomalous concentrations in placer haloes is pronounced for zirconium, yttrium, ytterbium, niobium, and tin [6]. This is clearly seen from Fig. 3a. The curve demonstrates a sharp rise in the concentration of these elements in the 0.01 mm and coarse classes. The better the sorting of the sediment, the more orderly is this increase. Two peaks of C/C_f for Zr, Y, Yb, and Nb are observed in classes of 0.02-0.01 and 0.1-0.05 mm, apparently reflecting initial differences in the grain sizes of accessory minerals accumulated in the heavy fraction.

The correlation of these elements among themselves and with titanium is different in the two grain size classes. In particular, in the class of 0.02-0.1 mm yttrium correlates better with titanium (0.75); in the class of 0.02-0.05 mm, with zirconium (0.72). We should note a fairly constant Y level in the light fraction of granular sediment class (an average of 11 g/ton). The maximum of these elements in the class of 0.02-0.005 mm stably enriched in accessory ore mineral is remarkable. It is possible that the various proportions of Zr with Y and Yb in coarse and fine silt material also reflect the existence of several varieties of zircons in the sediment, which is also confirmed by mineralogic investigations. In particular, zircons of the size class of 0.02-0.01 mm have a higher concentration of rare earth impurities. This possibility is supported by previous findings on seafloor sediments of the littoral shelf zone in this area [7].

In the balance sample some 73% of zirconium is associated with minerals of the heavy fraction, including just 20 % with zircon in the class of 0.1-0.05 mm, 27% with ilmenite, and some 26% with minerals of the heavy fraction in the class of 0.02-0.01 mm, not usually included in conventional mineralogic analysis. A substantial amount of zirconium is also disseminated in rock-forming minerals of the light fraction (14%) and terrigenous rock fragments (3%); some 10% is contained in coaly-clayey matter. Zr concentration increases slightly also in the fraction of $<1 \mu\text{m}$. That can be due to its presence in the form of hydroxides and adsorbed on colloids [9, 10]. In our case this is confirmed by a high Zr content (0.04%) in coalified organics.

The distribution pattern typical for the clastophilic group of elements is largely observed for tin as well (see Fig. 3a), apart from differences observed in the grain size spectrum of cassiterite in placers. Substantial quantities of tin are also established in other minerals of the heavy fraction: the highest concentrations are found in tourmaline and epidote (30 g/ton), pyrite (10 g/ton), and ilmenite. Generally, minerals of the heavy fraction account for some 90% of tin. After cassiterite, titanium minerals (ilmenite and leucoxene) are the most important carriers of tin, which account for some 27% of this metal concentrated in the heavy fraction (see Tables 1 and 2).

The higher Sn concentrations in the clay component of the sediment are important for understanding geochemical anomalies. They tend to gradually rise in the subdispersed clay phase and in coalified organics, indicating active sorption [16]. Other investigators [1] have noted the possibility of fixation of Sn-containing complex ions on

highly active sorbents. The secondary tin minerals hydrocassiterite and varlamovite concentrated in the dispersed phase may also be present in placer haloes.

The total tin balance in the sediments is described by the following distribution: tin in cassiterite, 66%; in other minerals of the heavy fraction, 25%; dispersed or in microinclusions in quartz and feldspar, 3%; sorbed by clay and coaly matter, 3%; sorbed by fine granular matter, ~3%.

The distribution of chalcophilic elements in the grain size spectrum of these metalliferous sediments is remarkable. Many of these (especially zinc, silver, copper, lead, bismuth, and molybdenum) are included regularly among associations of elements characteristic for these placers and their haloes [6, 17, 20]. The distribution of chalcophilic elements in the section of the metalliferous bed and the spatial variability trends along the course of the placer confirm their close paragenesis in metalliferous anomalies (see Fig. 1).

With special reference to a different placer (also located in a littoral-shelf zone) we established earlier that with increasing distance from the supply sources the anomalies become depleted of chalcophilic elements. We interpreted this as a sign of migrational geochemical zonality, reflecting decay of sulfidic minerals in mechanical scattering flows [3]. In this case, however, the situation is different. Despite the high KK of these elements, sulfidic minerals are quite rare in the heavy fraction of metalliferous deposits, which is attributed to the specifics of the development of placers as a result of redeposition and rewashing of crusts of chemical weathering.

Higher Cu, Zn, Ag, and Pb concentrations (due to microinclusions of sulfides that are observed at high magnifications in a polarization microscope) are typical for rock-forming minerals of feldspar and quartz. This accounts for the higher concentration of chalcophilic elements in the granular component of the sediments. For example, on average, feldspar of these samples contains, g/ton: Cu > 10, Zn 30-180, Pb n-10, Ag - 0, n; quartz Cu 5-12, Zn 30-150, Ag 0.25-0.6. A rise in Cu and Zn concentrations in fine psammitic material is due much less frequently to the presence of free grains of sulfide minerals — bornite, chalcopyrite, and sphalerite. Ag peaks in the psammitic component of the grain size spectrum of some of the specimens may be of similar origin: there, it rises by a factor of $n \times 10$ and $n \times 100$ above background levels.

The main distinctive trait in the distribution of the elements of this group in the grain size spectrum is the sharp rise of concentrations in the pelitic and especially subcolloidal fractions [2, 12, 19]. It is most pronounced for copper (KK up to 40) and zinc (KK up to 15). The presence of kaolinite in the clay fraction enhances copper sorption by several times. This is consistent with the conclusion drawn in [11] that kaolinite is capable of sorbing Cu almost entirely from solutions. A high copper sorptive capacity is also observed for coalified organic matter, which contains up to 200-280 g/ton of copper. There is no noticeable copper concentration by nodules.

Generally, the hydrogenic form of copper accounts in these sediments for 60 to 80% and more, including 15% of Cu extracted by acetate and the remainder by Chester's extract. The lowest copper concentrations (17 g/ton) are found in the technologically productive placer class; in fine siltstones its concentration doubles and in clays it is increased by almost a factor of 10. The total Cu balance according to these specifics can be described as follows: clay matter contains some 65%, minerals of the light fraction some 30%, and fine silt material some 5% in a sorbed form. The minerals of the heavy fraction account for 0.34-0.36 of the total Cu content.

The zinc balance is similar. Except for rare sphalerite and smithsonite grains, no proper zinc minerals have been found. Some of the minerals of the heavy fraction contain relatively higher quantities of Zn: especially tourmaline (>500 g/ton), epidote (>100 g/ton), and cassiterite (120 g/ton). Higher concentrations are also observed in nodules of pyrite (90-160 g/ton) and siderite (>350 g/ton). However, the main zinc concentration is clay-coaly matter, which accounts for some 63-69% of the total. Most hydrogenic Zn (from 50 to 97%) is extracted by acetate. Characteristically, about 30% of the zinc in individual and balance samples is associated with quartz and feldspar, with their sphalerite microinclusions and zinc disseminated in minerals (16-20%); about 10% is sorbed on fine silt matter. Just 1% of Zn is contained in minerals of the heavy fraction.

With some differences, the lead distribution is largely similar to that of copper and zinc [19]. There are no true lead minerals, except for isolated galena grains in horizons formed from the least weathered rocks; however, lead concentrations in the light fraction of the granular component are quite stable. The main lead concentrator among authigenic ore minerals is pyrite, which contains 80-370 g/ton of Pb.

The presence of hydrogenic manganese and iron forms can also affect the balance of mobile forms of lead. Sometimes the amount of lead in Chester's extract makes up 60 to 90% of the total quantity in the mobile form. Generally, coal-clay matter of these sediments contains some 45% of lead, rock-forming minerals some 35%, and rock fragments about 5%; the remainder is associated mainly with fine-silt, largely quartzose particles, apparently in a sorbed form. Less than 1% of the total lead is contained in minerals of the heavy fraction.

Silver balance is slightly different. Against the background of its sorption by pelitic particles, resulting in 30-35% of silver being contained in clay matter, the bulk of Ag (61-65%) is nevertheless associated with the light fraction — feldspar and quartz (especially colorless long-prismatic quartz). This also raises the share of silver contained in the technologically productive sediment class: over 50%, i.e., more than other chalcophilic elements by a factor of 1.5-2.

* * *

The foregoing data illustrate the diversity of the complex geochemical anomalies associated with placers in the littoral shelf zone. They reflect hypergenetic alternation of rock in supply area (in this case, deep chemical weathering of kaolin type), mechanical differentiation of clastogenic matter in the littoral zone, postsedimentary alteration of placers that resulted in intense sorption of hydrogenic forms of certain metals by coaly-clayey and fine-silt sediments, and accumulation of them in authigenic minerals.

These data confirm an earlier hypothesis [4, 7, 20] that only Zr, Ti, Sn, and B anomalies are clastogenic in these conditions (at the expense of true respective minerals). The former two elements reflect mechanical separation of material and are not included in the productive association of tin placers from the near-lying provenance sources. Only a few typomorphic elements of a tin placer are found in sediments as true minerals: tin in cassiterite, boron in tourmaline, and tungsten in wolframite. In a narrow range of settings on areas that directly supply the placer, and in the absence of deep chemical weathering of parent rocks (in this case, on the parts of the placer where the erosion cut reaches the lower horizons of the crust of weathering), certain chalcophilic elements of the initial ore paragenesis can be present in limited amounts in clastogenic form as sulfides. However, that form of chalcophilic element is typical only for initial placer paragenesis and usually does not exceed 1-2% of the total content.

More often, higher concentrations of chalcophilic elements in detrital matter are provided by microinclusions of sulfides in feldspar and quartz; sometimes they account for up to 50% and more of their gross content. Stable contents in quartz and feldspar regardless of fragment size (i.e., regardless of degree of their "opening" by fracturing of B, Mn, Ti, Sn, and other elements), suggests the possibility of atomic dissemination. The set of elements in detrital minerals present as an isomorphic impurity is much wider. These are Ga, Li, and Ba in feldspar and Y, Yb, Nb, and Sc in minerals of the heavy fraction (primarily zircon and ilmenite). Some of the Li, Be, and Ga is also contained in the isomorphic impurity in clay minerals. This fact may be responsible for the previously noted intermediate position of Sc, Ba, and Ga in sedimentary geochemical zonality series [6].

Metal sorption by clay matter, especially by kaolinite and coalified organics, has an important role in concentrating metallogenic elements and forming geochemical anomalies. A comparison of concentrations in the dispersed phase (relative to the granular component of the sediment) and in coal matter identifies the following nominal groups in these conditions: intense sorption — Cu, Pb, Co, Ni, and V; moderate sorption — Zn, Ag, Sc, and Ti (Nb); weak sorption — Bi, Li, and W (Zr, Y, Yb, and Sn). Mobile forms of chalcophilic elements sorbed by clay and organics are the main factors of the phenomenon important for prospecting: the development of above-ore Ag, Cu, Pb, and Mo anomalies in the recent layer of seafloor sediments over buried placer deposits (Fig. 4).

Siderite nodules are a powerful concentration of Co, Mo, Zn, and W. Complex Ti, Mn, V, and Sc anomalies are apparently associated with carbonified matter disseminated in the sediment. They are localized within submarine lows and flooded river beds — the "second titanium maximum" mentioned earlier in seafloor sediments — which thus provides no direct information on accumulation of ore minerals in placers.

These data indicate intense geochemical transformation of matter during the course of placer development. They also support specific inclusions concerning the nature of complex geochemical anomalies produced by placer accumulations of heavy minerals.

LITERATURE CITED

1. T. M. Amichba and N. I. Chistyakova, "The possibility of fixation of complex tin-containing ions on highly active sorbents," *Geokhimiya*, No. 11, 1647-1650 (1987).
2. E. N. Emel'yanov and V. N. Lukashin (eds.), *Geochemistry of Sedimentary Processes in the Baltic Sea* [in Russian], Nauka, Moscow (1986).
3. S. V. Grigoryan and N. G. Patyk-Kara, "Geochemical zonality of placers and its causes," *Dokl. Akad. Nauk SSSR*, 278, No. 5, 1192-1196 (1984).
4. V. A. Kuznetsov, *Geochemistry of Alluvial Lithogenesis* [in Russian], Nauka i Tekhnika, Minsk (1973).
5. A. A. Migdisov, "Titanium geochemistry in a humid sediment accumulation basin," in: *Chemistry of the Earth's Crust*, Vol. 1 [in Russian], Izd. Akad. Nauk SSSR, Moscow, pp. 336-351 (1963).
6. N. G. Patyk-Kara, "Geochemical criteria for exploration and evaluation of placers in the littoral shelf zone," *Sov. Geologiya*, No. 6, 74-83 (1987).
7. N. G. Patyk-Kara and K. V. Yablokov, "Geochemical features of seafloor sediments in the littoral shelf of Arctic seas as an indicator of sedimentation environments," *Litol. Polezn. Iskop.*, No. 3, 53-61 (1985).
8. V. V. Polikarpochkin, in: *Secondary Haloes and Dissemination Streams*, L. V. Tauson (ed.) [in Russian], Nauka, Novosibirsk (1976).
9. A. B. Ronov and A. A. Migdisov, "Main geochemical features of hydrolysate elements during the processes of weathering and sediment accumulation," *Geokhimiya*, No. 2, 131-158 (1965).
10. A. I. Samchuk and Yu. A. Sushin, "A study of solubility and complex formation in zirconium hydroxide-fulvic acid-water systems and the role of these processes in zirconium migration in natural waters," *Geokhimiya*, No. 4, 549-555 (1986).
11. A. A. Saukov, *Geochemistry* [in Russian], Nauka, Moscow (1975).
12. N. M. Strakhov, "Problems of the geochemistry of recent oceanic lithogenesis," *Tr. GIN*, Issue 292 (1976).
13. D. S. Thomas, "Applied geochemistry in mineral exploration," in: *Geology and Geochemistry of Ore Deposits* [Russian translation], Mir, Moscow (1977), pp. 210-222.
14. N. A. Shilo, *Fundamentals of the Theory of Placers* [in Russian], Nauka, Moscow (1985).
15. N. A. Shilo and N. G. Patyk-Kara, "Geochemistry of placers (geochemical aspects of matter concentration and dissemination in placers, geochemical evolution of placers, methods of placer exploration and evaluation)," *Tikhookean. Geologiya*, No. 2, 78-89 (1989).
16. J. T. Byrd and M. O. Andreae, "Geochemistry of tin in rivers and estuaries," *Geochim. Cosmochim. Acta.*, 50, No. 5, 835-845 (1986).
17. W. W. S. Yin, "Geochemical exploration for tin placers in St. Ives Bay," *Marine Mining*, 2, 59-78 (1979).
18. D. H. Loring, "Geochemistry of cobalt, nickel, chromium, and vanadium in sediments of the estuary and open gulf of the St. Lawrence," *Can. J. Earth Sci.*, 16, No. 6, 1196-1209 (1979).
19. D. H. Loring, "Geochemistry of zinc, copper, and lead in sediments of the estuary and the Gulf of St. Lawrence," *Canad. J. Earth Sci.*, 15, No. 5, 757-772 (1978).
20. R. M. Owen, "Geochemical exploration for marine minerals — placer deposits," *Oceanol. Int. Exhib. and Conf.*, Brighton, Vol. 1, 58-79 (1982).
21. R. M. Owen, "Geochemistry of platinum-enriched sediments: Applications of mineral exploration," *Marine Mining*, 2, 259-282 (1978).

MASS BALANCE IN THE SEDIMENTARY CYCLE OF KRIVOI ROG BASIN IRON DEPOSITS

D. A. Kulik and V. V. Pokalyuk

UDC 550.4:551.311.231(477)

The problem of the source matter during development of the Lower Proterozoic iron-silica schist bodies (ISSF) is discussed, based on the Saksagansk Formation in the Krivoi Rog iron ore basin. Based on new data on metamorphosed sialitic weathering horizons of the Krivoi Rog and the lithological characteristics of the Saksagansk Formation the mass balance has been calculated relating ancient weathering in the Archean granite-greenstone basement area to deposition of the iron-silica sediments. It was concluded that ancient weathering may have been completely responsible for simultaneous chemical precipitation of the entire iron and silica volume in the Saksagansk Formation. The depositional basin where ISSF developed was far from the area in which the sedimentary matter became mobilized during weathering. It may have been located even in a different climatic zone.

The Saksagansk iron ore formation of the Krivoi Rog Basin is a Lower Proterozoic iron-silica schist formation (ISSF) [18]. It is assumed that weathered Archean basement rocks were its main source during its development [2]. It was also assumed that a purely terrigenous source would have been insufficient and that the main source of iron and silica came either from volcanic-hydrothermal processes [39] or from waters of the early Proterozoic ocean (the accumulative theory by Mel'nik [29]).

Our aim here is to clarify whether it would be possible to account for the deposition of the Krivoi Rog Basin iron ore formations only through weathering of Archean granite-greenstone basement rocks and whether these processes occurred simultaneously, or had been separated in time. Solution of these problems would facilitate the establishment of specific paleotectonic and paleofacies models of sedimentary iron accumulation in Lower Proterozoic iron ore basins.

The following facts are listed to help establishing the terrigenous source of the dominant portion of iron and silica of the ISSF in the Krivoi Rog Basin:

1. The Saksagansk Formation lies conformably on metaterrigenous deposits of the Skelevatsk Formation, representing the final member of a sedimentary facies sequence, stretching from terrigenous coarse detrital deposits to finely dispersed basin deposits (transgressive sequence [36, 40]). A genetic connection was established in this sequence between iron-silica deposits and weathering horizons.

2. Approximately 30% of the formation's volume is composed of so-called schist horizons (Fig. 1). An important portion of these is composed of terrigenous metapelitic matter.

3. Monomict quartz metasandstones, widespread Al-schists and metamorphosed weathering horizons in the pre-Saksagansk section of Krivoi Rog reflect intensive chemical weathering in land area and the high grade of sedimentary differentiations during the period that preceded ore formation. This indicates that intensive iron and silica loss took place from the weathering horizons.

4. The section of the Saksagansk Formation does not contain effusive products, clear indications of volcanism and traces of fumarole-solfatara activity. This suggests the absence of a direct connection between deposition of the iron-silica matter and volcanism.

Institute of Mineral Geochemistry and Physics, Academy of Sciences of the Ukrainian SSR, Kiev. Translated from *Litologiya i Poleznye Iskopaemye*, No. 2, pp. 36-49, March-April, 1990. Original article submitted January 4, 1989.

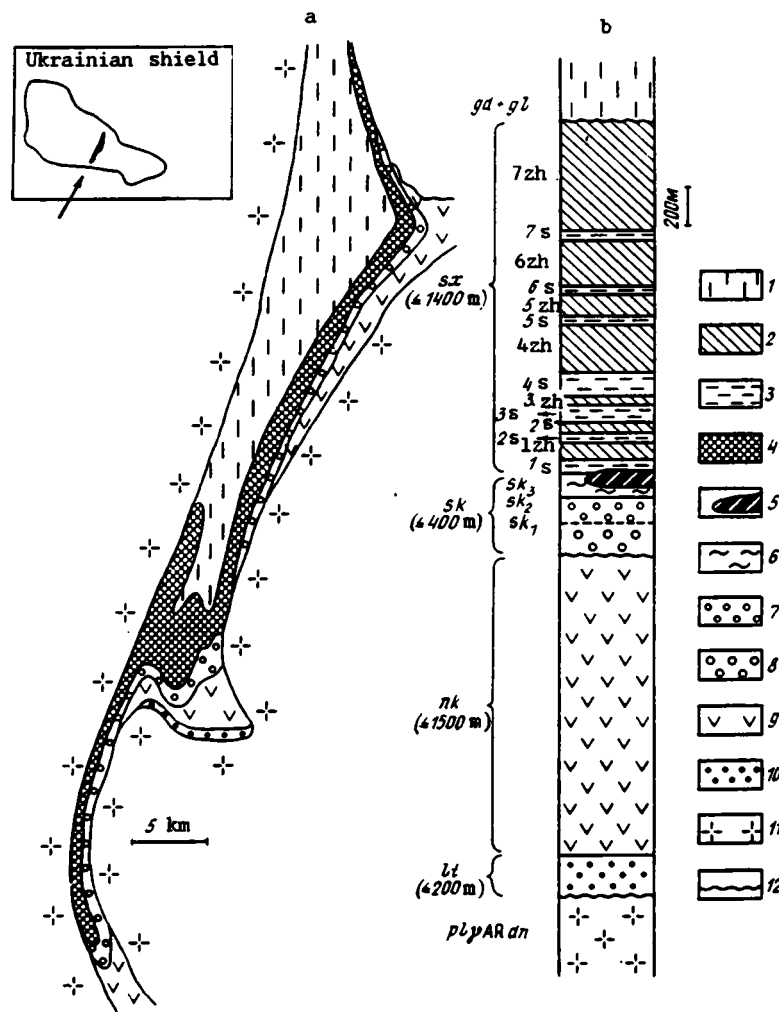


Fig. 1. Geological outline of the Krivoi Rog basin (a) and composite stratigraphic column (b) of the Saksagansk Ore Formation and the underlying metasedimentary and metavolcanic rock complexes (based on [3] and additional data). 1) metaterrigenous and metachemogenic-terrigenous deposits of the Gdantsevsk and Gleevatsk Formations (gd + gl) — carbonaceous quartz and biotite schists, meta-sandstones, dolomites, metaconglomerates, etc.; Saksagansk Formation (sx): 2) iron-bearing horizons (silicate-magnetic iron quartzites, hematite-magnetite-bearing jaspilites, etc.); 3) schist horizons (quartz-chlorite-biotite schists, ore-free quartzites, etc.); 4) ISSF of the Saksagansk formation; Skelevatsk formation (sk): 5) metaultrabasites (talc-chlorite, talc-chlorite-carbonate schists, etc.); 6) quartz-sericite schists and biotite, quartz, sericite-schists, etc.; 7) feldspar-quartz metasandstones, etc.; 8) essentially oligomict metaconglomerates and meta-gritstones, etc.; 9) basic and intermediate metavolcanic rock of the Novokrivoirog Formation; 10) metasandstones and metagritstones of the monomict quartzitic Latovsk Horizon (Formations); 11) plagioclase granites of the Archean basement (plγARdn); 12) traces of stratigraphic unconformity.

Data in recent years on the lithologic characteristics of Saksagansk Formation iron-silica rocks and conclusions on metamorphosed weathering horizons of the pre-Saksagansk section of the Krivoi Rog basin allow a more detailed review of the mass balance in the early Proterozoic sedimentary cycle, including iron and silica mobilization, their transport and sediments in the Krivoi Rog basin.

TABLE 1. Average Chemical Composition, Pre-Saksagansk Complexes

Bed (formation)	Rock	Number of analyses in the samples	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	Fe	MnO	CaO	MgO	P ₂ O ₅	K ₂ O	Na ₂ O	SO ₃	CO ₂	Calcination loss	H ₂ O	Total	Source
Saksagansk formation	% average	—	46.6	0.19	4.87	28.02	11.81	28.8	0.08	0.9	1.67	—	1.59	0.34	—	3.19	—	—	100.00	[18]
Skelevatsk formation	Quartzsiderite schists (phyllites)	12	63.32	0.74	17.84	1.47	3.48	—	0.03	0.56	2.06	0.04	6.03	0.81	0.23	0.17	3.85	0.06	100.69	Data by authors
	Metasandstones	10	75.55	0.40	11.5	0.74	2.15	—	0.038	2.04	1.39	0.05	3.11	0.61	0.36	0.25	2.18	0.12	100.49	
Metaeluvial matter from metavolcanites	Metaeluvial zones IV l-chl-ser schists	1	55.3	0.92	18.93	2.50	10.0	—	0.19	1.00	2.40	0.26	0.20	4.90	0.08	0.70	3.93	—	101.31	[17]
	III chl-bi schists	4	54.88	0.62	14.55	2.16	9.54	—	0.13	1.73	7.47	0.099	0.43	4.34	0.06	0.97	5.26	—	102.24	
	II q-pl-act rock	3	51.18	1.03	14.30	2.21	11.42	—	0.14	3.96	8.10	0.113	2.11	1.69	0.05	0.94	5.15	—	102.39	
	I massive amphibolites	5	52.25	0.90	13.77	2.24	11.17	—	0.14	5.39	7.00	—	1.98	3.02	—	0.42	2.3	—	100.58	
Novo krivai rag formation	Metavolcanites of basic intermediate composition	99	51.32	0.90	14.36	2.80	9.08	—	0.17	5.96	7.30	0.103	1.72	2.42	0.07	0.89	2.99	0.18	100.26	Data by authors
Latovsk horizon	Metasandstones and metagritstones	18	86.9	0.09	8.30	0.19	0.70	—	0.008	0.26	0.30	0.027	1.82	0.25	0.02	—	1.15	—	100.01	Same
Metaeluvial matter from plagioclase granites, drillhole 20630 (Rakhmanovo)	Metaeluvial zones IV q-ser schists (most thoroughly transformed metaeluvial samples)	1	70.05	0.37	19.88	—	0.44	—	0.002	<0.10	0.17	0.14	5.18	0.53	<0.02	ab-sent	2.82	—	99.66	[27]
	q-ser, ser-q schists	6	72.52	0.34	18.12	—	0.58	—	0.004	<0.10	0.28	0.05	4.82	0.46	0.03	"	2.48	—	99.78	
	B chl-q-ser and chl-ser-q schists	3	71.11	0.283	15.88	0.55	3.07	—	0.013	0.12	1.54	0.04	3.68	0.37	0.17	"	2.82	—	99.64	
	A bi-q-ser, chi-q-ser schist	6	69.68	0.282	15.98	0.94	3.12	—	0.030	0.26	2.29	0.036	3.87	0.46	0.03	"	2.75	—	99.41	
	Sericitized pl-granites	2	70.29	0.275	16.18	0.61	2.17	—	0.031	1.04	1.68	0.03	3.28	2.45	<0.02	"	1.48	—	99.54	
	"fresh" pl granites	9	70.26	0.279	15.66	0.64	2.38	—	0.029	1.51	1.29	0.043	2.23	3.69	0.03	"	1.65	—	99.69	
Plagioclase granites of Saksagansk river		12	69.96	0.34	15.16	1.24	2.56	—	0.054	2.18	1.16	0.05	1.54	4.78	0.06	0.17	1.62	0.70	100.13	[4]

TABLE 2. Loss of Iron and Silica during Pre-Saksagansk Weathering of Plagioclase Granites and Metabasites

Parameters	Component	Plagioclase granites $\rho = 2.69 \text{ g/cm}^3$	Metabasite $\rho = 2.80 \text{ g/cm}^3$
Source composition in 1 m^3 of unaltered rocks, kg/m^3	FeO	64,02	254,2
	Fe_2O_3	17,22	78,4
	Fe^{2+}	49,74	197,51
	Fe^{3+}	12,05	54,88
	SiO_2	1889,99	1436,96
	Si	882,06	670,63
Loss from the upper eluvium zone, kg/m^3	$\text{Fe}_2\text{O}_3 + \text{FeO}$	73,12(90)	99,78 (30)
	$\text{Fe}^{2+} + \text{Fe}^{3+}$	55,61	75,72
	SiO_2	472,50(25)	431,11(30)
	Si	220,52	201,20

The stratigraphic section of the Krivoi Rog synclinorium (Fig. 1) is subdivided in the following fashion (from bottom to top): 1) Late Archean plagioclase granite basement; 2) Latovsk quartz horizon; 3) sedimentary-volcanic Novo Krivoi Rog Formation; 4) clastic Skelevatsk Formation; 5) essentially chemogenic Saksagansk (iron ore) Formation; 6) chemogenic-clastic Gdantsevsk Formation; 7) the clastic Gleevatsk Formation [3, 42]. Two additional horizons of residual metamorphic weathering horizons occur in the pre-Saksagansk section: the Predlatovsk Prednovokrivorozhsk (overlying the basement plagioclase granites) and the Predskelevatsk horizon (overlying the plagioclase granites of the Novo Krivoi Rog Formation). The metamorphic products of these weathering horizons have been penetrated by drillholes and mining operations in the large areas of the Krivoi Rog basin and have been discussed repeatedly in the literature [4, 5, 9-11, 13, 16, 17, 20-22, 24, 27, 28]. Most of the researchers think that weathering did not reach the stage when free Al-bearing minerals formed in the weathering horizons. Well-developed kaolinitic zones, however, did form.

In the quantitative evaluation of the intensity of the chemical weathering processes it is important to determine the maximum values of element loss that occurred during formation of the weathering crust in the highest eluvial zones. The following data relates to the most complete sections under consideration. Thus, the section in drillhole No. 20630 of the southern Krivoi Rog area [27] reveals the Predlatovsk-Pre-Novo Krivoi Rog horizon. The following zones (from bottom to top) were present in this section: I — plagioclase granites of biotite-quartz-fresh plagioclase; II — gradual transition from granites to biotite-quartz-sericite schists (1 m); IIIA — biotite-quartz-sericite schists, rarely chlorite-sericite-quartz schists (6 m); IIIB — chlorite-quartz-sericite schists, chlorite-sericite-quartz schists (4.5 m); IV — quartz-sericite and sericite-quartz schists (6 m). These zones, based on a number of criteria, are comparable with zones of unmetamorphosed weathering zones such as: unaltered rocks (I), disintegrated and initially leached substances (II), illitic zone (III) with illitic (IIIA) and kaolinite-illitic (IIIB) subzones, kaolinitic zone (IV). The average chemical composition of the zones is given in Table 1.

The best method of quantitative evaluation of the mobile elements in metamorphosed weathering horizons according to a number of authors, is provided by the calculation in terms of the least mobile element [10, 11, et al.]. The ratio between the concentrations of such an element (oxygen) in the altered rock and concentration in unaltered rock characterizes the magnitude of element loss/gain of other elements. Usually Al or Ti is used as the tracer element; these are the most inert elements during weathering processes. Al is the most favored, as its concentration values display the least fluctuations. The low level of Al and Ti mobility in Precambrian weathering horizons is confirmed by the stable Al/Ti ratio as traced upward in the weathering horizon. This profile starts at the bottom with unaltered bedrock and concludes at the top with moot altered residual weathering products [11]. In the investigated metamorphosed eluvium of plagioclase granites the Al/Ti ratio remained stable within the section. Thus, the use of element-tracer method in this instance is proficient and indicates an 89% iron loss from the upper meta-eluvial zone, when compared with the original concentration in unaltered plagioclase granites. It also shows a 24.8% silica loss.

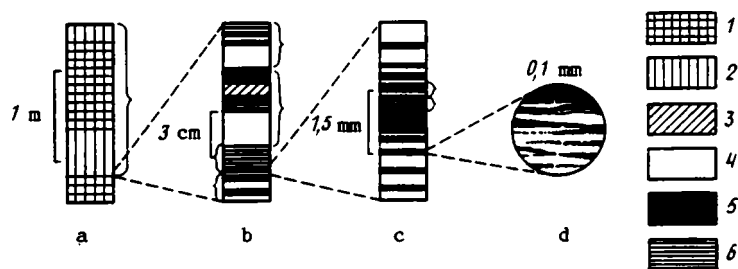


Fig. 2. Composition of polyrhythmic layering of iron-bearing quartzites [a) macrolayer; b) meso-layer; c) microlayer; d) microlayering]. 1-2) macrolayer, composed of carbonate-magnetite and magnetite quartzite layers, respectively; 3) silicate layer; 4) quartzite meso- and microlayers; 5) magnetitic meso- and microlayer; 6) silicate quartz-ore and ore-quartz meso- and microlayer. Brackets with figures refer to macro-, meso-, and microrhythms.

Magnitude-wise, these data agree with loss of the components from kaolinitic zones of young non-metamorphosed weathering horizons of granitoid rocks [6, 38, et al.]. In these, the iron oxide loss ranges between 48-81%; 1.1-1.8 times less than in the meta-eluvium of plagioclase granites. The silica loss amounted to 28-48% (correspondingly 1.1-2.0 times greater). These differences may be related to the more active filtration, higher acidity and reducing character of infiltrating waters during formation of ancient weathering horizons on the plagioclase granites.

Values of silica loss (25%) and iron oxide loss (90%) from upper units of the ancient eluvium of the plagioclase granites have been employed in additional calculations.

The most complete meta-eluvium profile over metavolcanites of the Novo Krivoi Rog Formation has been described from the northern Saksagansk area of the Krivoi Rog basin, in the Lenin Mine [17]. The following zones were recognized here: I — massive amphibolites; II — quartz-plagioclase-actinolite rocks (maximum 40-50 m); III — chlorite-biotite schists (20-25 m); IV — quartz-chlorite-sericite schists (maximum 30-35 m). Before metamorphism, these zones included unaltered rocks, leached amphibolites, montmorillonites and kaolinites. Table 1 gives their chemical composition.

Calculation of mass balance in this profile, based on the Al-tracer indicates maximum loss of Si (22.8%) and Fe-silicates (32%) in the upper zone, when compared with source rock values. Similar values, based also on the Al-tracer, were provided in works by Gershoig and Kaplu [9] for the upper meta-eluvial zones on epidiorite dikes at the contact with rocks of the Skelevatsk formation in "Communard-Victory" Mine. These values were 31.4% and 32.1%, respectively. Based on these data, the values of silica and iron oxide loss from the upper meta-eluvial zone were calculated as 30% and 30%, respectively. Dodatko [15] provided somewhat different component loss values from the upper meta-eluvial zone overlying amphibolites of the Novo Krivoi Rog Formation. These values were calculated by the concentration method, using the reduced rock density (based on calcite content in the meta-eluvial zones). The SiO_2 value was 41.8%, the $\text{Fe}_2\text{O}_3 + \text{FeO}$ value was 46.1%. It is noted that our values apparently are significantly lower than the actual maximum loss values during weathering of volcanic rocks of the Novo Krivoi Rog Formation. This is indirectly indicated by the fact that in the unmetamorphosed, bleached kaolinitic weathering horizons over basic rocks, the silica and iron loss from the upper (kaolinitic) zones reaches significantly higher values. Thus, silica loss from the upper kaolinitic zones is 54%, iron loss 85.4%, in the pre-Jurassic white kaolinite weathering horizon of the Ubagan region basalts in the Turgai Basin. The loss in the ferrimontmorillonite zone of the same weathering horizon was 28.6%, respectively, 31.8%.* The last values are in complete agreement with the values of loss from the upper portion of old eluvium over metavolcanic rocks.

*Calculated by the Al_2O_3 constant-method, based on Mikhailov and Petrovskaya [32].

TABLE 3. Values of m_{Fe} and m_{SiO_2} of Microlayered, Mixed, and Ore Mesolayers of the Iron Horizons of the Saksagansk Formation in the Krivoi Rog basin

Mesolayer types	Number of the iron horizon	Number of calculations	m_{Fe} , mg/cm ³	Variation coefficient, m_{Fe}	m_{SiO_2} , mg/cm ³	Variation coefficient, m_{SiO_2} , %
Quartzitic	1,2,4	63	17.6	82	218	107
	5,6,7	67	9.1	75	119	62
Mixed ore-quartzite	1,2,4	30	33.6	60	73	78
	5,6,7	40	33.3	96	89	90
Mixed quartz-ore	1,2,4	54	50	145	19.7	62
	5,6,7	35	47.5	58	49	81
Ore	1,2,4	61	77	133	10.4	106
	5,6,7	35	82	100	26.5	107
Most likely values of fresh sediments	1-7	-	20-30	-	40-60	-

TABLE 4. Calculated Deposition Time of the Saksagansk Formation

Stratigraphic level	Average thickness, m	Ratio of schist layers, in %	Time of deposition million years
Upper part of formation			
5zh + 6zh + 7zh	650	24.3	4.89
5s + 5zh + 6s + 6zh + 7s + 7zh	775	25.9	5.79
Lower part of formation			
1zh + 2zh + 3zh + 4zh	310	15.6	2.74
1s + 1zh + 2s + 2zh + 3s + 3zh + 4s + 4zh	595	45.6	3.76
Total formation	1370	34.45	9.55

One may now calculate approximate values for the iron and silica, that were lost from unit volumes of weathered plagioclase granites and greenstone rocks. Using the average plagioclase granite density value (2.69 g/cm³) and their iron oxide composition ($Fe_2O_3 + FeO = 3.02\%$), their mass in 1 m³ rock was 81.24 kg, calculated for native Fe, 61.79 kg. 90% of this value (accounting for iron loss from the upper plagioclase granite zone), equals 55.61 kg. A similar calculation for the metavolcanites of the Novo Krivoi Rog Formation (density = 2.80 g/cm³; $Fe_2O_3 + FeO = 11.88\%$) indicates that iron loss from 1 m³ rock equaled 75.72%. The same method is used for calculating the silica loss value (Table 2).

Further analyses require calculation of the total iron and silica volume, deposited in the Saksagansk Formation, and its deposition rate.

The Saksagansk Formation, first defined by Bevtsev [1] as the middle formation (K_2), unconformably overlies rocks of the Skelevatsk Formation. It contains huge iron quartzite and rich iron ore deposits [3, 8]. The formation consists of a few large cycles, each represented by schist and iron horizons. The most complete, 1400 m thick section of the formation in the central basin area (Fig. 1) includes seven iron and seven schist horizons, with a total thickness of 1400 m. Laterally and in dip direction the composition and thickness of iron and schist horizons undergo changes until the units completely wedge out (second and fourth iron, and fifth and sixth schist horizons). In all, the Saksagansk Formation is composed of 70-80% iron-silica rocks with very high iron (25-40%) and silica (40-60%) content, along with much lower Al_2O_3 , MgO, CaO and other petrogenic oxide content. A small portion in the lower part of the formation is composed of phyllite-like ("aspidic") schists within the first-to-the fourth schist horizons. A number of major papers [7, 19, 31] provided detailed petrographic and geochemical descriptions of characteristics of the iron and iron-free rocks in the Saksagansk formation. The average thickness of the iron rocks in the Saksagansk Formation is 1 km and the average iron content in them is 30%, that of silica, 46% (Table 1).

TABLE 5. Mass Balance Between Weathering of Plagiogranite-Greenstone Rocks and Sedimentation in the Krivoi Rog basin

Weathered rock	Component	ρ_i , kg/m ³	q_i , mg·cm ⁻² · yr ⁻¹	Imbalance $\left(\frac{M_i(\text{wea})}{M_i(\text{dif})}\right)$	S_{wea} , km ²	S_{wea} S_{bal}
Plagiogranites	Fe(solution)	55.6	20	1	1.8 · 10 ⁵	36,0
	SiO ₂ Terri- genous	472.5	30	5,6		
	clastics	2120	16,6	45,9		
Basites	Fe(solution)	75.7	20	1	1,3 · 10 ⁵	26,4
	SiO ₂ Terri- genous	431.1	30	3,7		
	clastics	2036	16,6	31,9		

Note. 1. Bulk density (kg/m³) of equal the reduced bulk density of the upper zone of the residual eluvium. Calculated by the constant-Al method (V. S. Pevzner). 2. Average deposition rate of the terrigenous clayey matter for the entire time range of Saksagansk Formation, calculated by the ratio $v_{\text{Fe}}/C_{\text{Fe}} = v_{\text{clast}}/C_{\text{clast}}$; where C_{Fe} = average Fe concentration in the Saksagansk Formation (Table 1), C_{clast} = its average clastic content, assumed to be 25%. C_{clast} was calculated by the ratio of petrogenic oxides in phyllites, based on the average Al₂O₃ content in the Saksagansk Formation (Table 1), assuming that the total Al weight is represented by terrigenous Al-silicates.

Sections of the schists and iron horizons usually display authigenic mineral zonation. Most completely this is reflected in the minimally metamorphosed rocks in the following sequence (from bottom-to-top from the center of the schist horizon to the center of the iron horizon): phyllite schists — phyllite schists with quartz layers — chlorite-biotite quartzite schists* — magnetite — carbonate-chlorite quartzite schists — chlorite-magnetite-carbonate schist quartzites — carbonate-magnetite quartzites — magnetite quartzite — hematite-magnetite jaspilites. Further upward in the direction of the overlying schist horizon, this succession is reversed. This zonality in the Saksagansk Formation is expressed as a higher-order cycle over which lower-order cycles are superimposed. This occurs down to the level of laminar structures that are characteristic of iron quartzites and schists (Fig. 2).

Ore, quartzitic and composite ("meso")-laminae, 1-10 mm thick and visible with the naked eye, usually are composed of alternating pairs of laminae, fractions of one mm thick, that contain more or less ore minerals. Lamination is especially well expressed in the enclosed ore-quartz mesolaminae (in jaspilites). Their detailed study [26] indicated that lamina alternations resulted in microrhythmic patterns. In all probability, each microrhythm was laid down in an annual cycle and reflect the alteration of dry and humid or hot and cold seasons. The microrhythms in the enclosing mesolaminae are 0.2-0.8 mm thick (average: 0.3 mm). Microrhythms occur in ore mesolaminae and in certain "anomalous" quartz mesolaminae. These can not always be interpreted as being of seasonal origin; the layers have often undergone significant diagenetic changes [25].

Thus by measuring the thickness and mineral composition of the microlaminae in the composite ore-quartz mesolaminae, one theoretically may use them in calculating sedimentation rates of iron-silica deposits during deposition of the Saksagansk Formation. This method was first employed by Trendall [45] for Hamersley Basin iron quartzites of Western Australia. We have measured the following dimensions under microscope in transparent thin or polished section: 1) thickness of the entire composite mesolamina, H; 2) number of microrhythms in the mesolamina, n; 3) thickness of the microrhythm ($h = H/n$); 4) use of the standard preparation method in establishing the volume percentages of magnetite (a_{mag}), hematite (a_{hem}), siderite (a_{sid}), and quartz (a_{q}) in the mesolamina; 5) recalculation of

*Quartzite schists are thin interlayered schist, ore, and quartz layers with schists predominating. The schist quartzites are the same but include predominant quartz and ore layers.

volume composition of minerals in terms of weight ratios of Fe, SiO₂ and other oxides [25, 26]; determining the iron composition (m_{Fe}), silica volume (m_{SiO_2}), within 1 cm² of a microlamina (the volume of this microunit numerically expressed as h ; the thickness of the microrhythm, in cm). If each microrhythm was deposited in one year, the deposited amount is expressed as v_{Fe} and v_{SiO_2} — the average sedimentation rates of iron and silica, correspondingly.

The volume of iron's m_{Fe} value was calculated, based on composite, quartz and ore mesolaminae of all iron horizons of the Saksagansk Formation (Table 3). The value was similar to values found in the iron horizons of the lower and upper parts in the formation. Diagenetic loss of iron may have occurred from the youngest quartz mesolaminae, while silica loss occurred from the ore mesolaminae [25]. The best estimate for the iron sedimentation rate at the time of deposition of the Saksagansk Formation was 20–30 mg/cm²/yr; for silica deposition: 30–60 mg/cm²/yr.

The maximum iron deposition rate value (20 mg/cm²/yr) may be utilized for determination of the entire time span of deposition of the Saksagansk Formation [25]. The corresponding mean thickness of the microrhythm (0.2 mm) allows determination of the deposition time of the iron horizon if it may be assumed that, as most likely, depositional breaks are absent within a given horizon. Significant uncertainty, however, exists in calculating the deposition rate of the silicate layers of iron quartzites and schist horizons. However, the likely catastrophic origin of the schist layers appears to suggest a higher deposition rate in comparison with iron quartzites and jaspilites proper. At the same time, scours may occur in beds of the schist horizon. Values in Table 4 display estimates based on a 2 mm/yr average deposition rate for the schist beds in the iron horizons and 0.5 mm/yr for the schist horizons. The depositional time span of the Saksagansk Formation is on the order of 10 million years, in conformity with estimates of 5 million years, by Trendall for the Brokmén iron horizon, thickest horizon within the Hamersley Formation.

The volume of iron deposited in the Krivoi Rog basin during Saksagansk time is of great interest. The length of the Krivoi Rog basin proper from Ingulets Mine to the northern part of the Annovsk region is approximately 100 km. Similar to the Hamersley Basin of Western Australia, unaffected by erosion and tectonic deformations [44], length/width ratio of the Krivoi Rog basin is 2:1. This also corresponds to the approximately 30:1 ratio between the width of the basin and the thickness of its iron ore formations. The area of sedimentation of the Saksagansk Formation therefore was 5,000 km² and its volume, based on an average 1 km thickness, 5,000 km³. The average iron content of 30% and rock density was approximately 3 g/cm³. Therefore, the total iron content was of the order of 5·10¹² tons. Annually, iron deposition occurred at a rate of 20 mg/cm²/yr, resulting in the deposition of a minimum of 10⁶ tons of iron over a basin floor area of 5·10³ km². The discrepancies between volume estimates may be explained by uncertainties concerning schist deposition rates in the Saksagansk Formation.

By now, we have obtained all values needed in the construction of a mass balance model of the early Proterozoic terrigenous sediment accumulation cycle in the Krivoi Rog basin. The assumption of synchronous iron deposition processes and its loss from the weathering horizon means that the iron volume that was deposited in the basin during time span t ($M_{Fe_{dep}}$) equals the volume of iron, dissolved and transported from the weathering horizon during this time span ($M_{Fe_{wea}}$). The general equation follows:

$$M_{i_{wea}} = M_{i_{dep}}, \quad (1)$$

where M_i = the volume of components (Fe, SiO₂, clastics, etc.).

It is clear that the balance (1) can be rewritten in the following manner:

$$S_{eros} = dp_i = S_{bas} v_i, \quad (2)$$

where S_{eros} is area of erosion; d is the linear weathering rate corresponding to [35], corresponding to the average denudation rate of continental areas (100 m·yr⁻⁶ [23]); p_i is volume of components lost from a unit volume of weathered rock (cf. above); S_{bas} is area of the Greater Krivoi Rog basin (5·10³ km²); v_i is absolute depositional speed of components in the basin, mg/cm²·yr. Only the area of weathering S_{eros} in Eq. (2) is an unknown factor. By using values p_i and v_i for iron (Table 5) in the balance equation (2), we get a value of 1.8·10⁵ km². This value coincides with the area of the Pre-Dnepr Block (1.2·10⁵ km²) and is significantly smaller than granite-greenstone areas, such as the Yilgrarn Block, Western Australia (over 10⁶ km² area) or the Archean Ungawa craton, Canadian Shield [44]. The ratio between area of erosion and deposition (30, in this instance) is close to values, found in present-day humid areas (values of 20–40 [40]). Thus, consistent values were obtained on erosion area/deposition area ratios, in complete

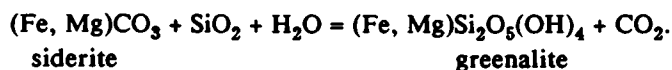
agreement with contemporary values. Therefore, it is assumed that humid weathering of plagioclase granite-greenstone regions under conditions of a reducing, oxygen-free, carbon dioxide atmosphere without hydrogen sulfide, may completely guarantee the synchronous settling of iron in ISSF of the Krivoi Rog and similar other basins.

If S_{eros} equals $1.3 \cdot 10^5$ and $1.8 \cdot 10^5 \text{ km}^2$, silica balance calculating (Table 5) indicate that in the terrigenous cycle during iron accumulation a surplus of soluble silica is mobilized on land; its amount is 3.7-5.7 times the amount that is deposited with the iron ore formations. This means that weathering in plagioclase granite-greenstone regions guarantees synchronous deposition of silica in the ISSF.

The greatest difficulty is created by the large imbalance (ranging between 32-46 times) with regard to the terrigenous clastic matter (Table 5), received from formula (1). This involves the assumption that the iron balance is satisfied. If the clastic matter is deposited in the area of the soluble Fe and SiO_2 , no iron-silica rocks may form, as the their clastic content hardly exceeds 20-25%.

Two models may clarify this balance:

1. The mobilization processes of Fe and SiO_2 on land were separated by a period from the deposition period of the ISSF. This intervening period was a shorter or longer accumulation phase of dissolved Fe and SiO_2 forms in the ocean, as assumed by Khodyush [41], Mel'nik [29, 30] and others. Recent calculations of the iron volume (10^{15} tons) in the ISSF [43] allowed an independent check on the reliability of the discussed mass balance scheme. If the oceanic volume in the early Proterozoic equaled the present-day value ($0.9-1.0 \cdot 10^{24} \text{ g}$), it can be then calculated that in agreement with accumulative concentration theory, concentration of the dissolved forms of bivalent Fe before the start of deposition of the ISSF was at least 0.8-1.0 g/liter (in the case of SiO_2 : at least 1.3-2.0 g/liter). Neither value could have been attained by purely physicochemical means. The stable concentration of soluble $\text{Si}(\text{OH})_4$ in ionic form does not exceed 100 mg/liter (that of the solubility of amorphous silica) [33], but the excess precipitates quickly in colloidal form. The Fe^{2+} solubility is buffer-controlled [30]:



This sustains Fe^{2+} concentrations on the order of a few to tens of milligrams per liter, at $p_{\text{CO}_2} = 0.1-0.01 \cdot 10^5 \text{ Pa}$. The iron excess at lowered p_{CO_2} precipitates in silicates; at higher p_{CO_2} values, in carbonates.

Consequently, during deposition of ISSF, the dissolved iron and silica in the ocean were recycled at least 30-50 times. This indicates that the accumulative calculation model is not useful.

In our view, the second model is more promising.

2. The terrigenous mobilization processes of Fe and SiO_2 proceeded simultaneously but occurred in separate areas. In this case the ocean did not accumulate iron and silica prior to accumulation of the ISSF. Rather, it was the buffer that "filtered them out" from the terrigenous and volcanic matter and transported them to upwelling sites, lagoons or other localities, favorable for chemical sedimentation of iron-silica deposits.

Relics of thick (10 km or greater) terrigenous (schist and gneiss) units occur beyond the limits of the Krivoi Rog basin, distributed over an area that at least equals the area of that basin. They are of the same age as the ISSF.

The thick (>10 km) metaterrigenous Ingulo-Inguletsk Series occurs west of the Krivoi Rog-Kremenchug ISSF area.

Various workers correlated these beds to the iron ore section of the Saksagansk Formation. In certain works they were considered younger [7, 14], in others older [37] than that section. Traditionally, these beds have been correlated exclusively with the metaterrigenous complexes. The possibility was not considered that the iron-silica deposits of the Saksagansk Formation and the metaterrigenous beds of the Ingulo-Inguletsk Series may be of the same age, formed in different depositional facies. Due to its great thickness and distribution area, the Ingulo-Inguletsk Series deposits may be entirely correlatable with terrigenous landslide-slump complex sediments that formed simultaneously with the iron accumulation in the Krivoi Rog basin. This view deserves attention, for it explains what happened to the huge volume of terrigenous matter, transported from land areas during weathering of granite-greenstone areas, while deposition of the Saksagansk Formation, a subunit of the Krivoi Rog Series, had taken place.

If it appears that deposits of the Ingulo-Inguletsk Series are not synchronous with the ISSF, this may mean that they were deposited in areas of slump (landslide) sedimentation; therefore areas of weathering and Fe and SiO_2 mobilization were located at significant distances from the ISSF depositional basins, possibly in a separate climatic belt. This assumption appears to be confirmed by M. N. Korzhnev: practically all large Lower Proterozoic iron ore

basins are distributed along a large circle with the circumference of about two-thirds of the present Earth radius, within the limits of the ancient Pangea in the reconstruction of Gorai [12]. As all the ISSF are characterized by the predominance of chemical sedimentary rocks over clastic rocks, such a basin distribution pattern may indicate that the ISSF were deposited in a more arid climatic belt, as mobilization of Fe and Si from weathering horizons obviously occurred within humid zones, located at higher or lower latitudes.

The present model, finally, does not exclude the possibility that soluble Fe and Si may have been derived not only from terrigenous but also other sources; for examples, from the volcanic-hydrothermal systems of midoceanic ridges [34]. However, the geochemical iron cycle in this and other Precambrian volcanic processes still remains to be evaluated.

LITERATURE CITED

1. Ya. N. Belevtsev, "Stratigraphy and tectonics of the Krivoi Rog basin," *Sov. Geol.*, No. 11, 3-24 (1946).
2. Ya. N. Belevtsev, "Deposition of rocks of the Krivoi Rog Formation," *Sov. Geol.*, No. 23, 44-53 (1947).
3. Ya. N. Belevtsev, and R. Ya. Belevtsev, *Geology and Iron Ores of the Krivoi Rog basin* [in Russian], Naukova Dumka, Kiev (1981).
4. P. M. Bondarenko, B. I. Goroshnikov, P. M. Kuleshov, and V. N. Kucher, "The interrelationship between the Krivoi rog metamorphic series and the Saksagansk plagioclase granites," *Tr. N.-i Metallurg.-Mining Inst., Ser. Geol.*, No. 2, 132-142 (1959).
5. E. T. Bobrov and I. G. Shipakina, "Archean metamorphosed weathering horizons of Krivoi Rog and reconstruction of their formation conditions," in: *Continental Unconformities and Weathering Horizons in the Precambrian of the East European and Siberian Platforms* [in Russian], Nauka, Moscow (1985), pp. 132-148.
6. N. I. Butsinskaya, *Ancient Weathering Horizon of the Northwestern Part of the Ukrainian Shield* [in Russian], Naukova Dumka, Kiev (1972).
7. Ya. N. Belevtsev, G. V. Tokhtuev, A. I. Strygin, et al., *Geology of the Krivoi Rog Iron Ore Deposit* [in Russian], Izd. Akad. Nauk Ukrain. SSR, Vols. 1 and 2 (1962).
8. Ya. N. Belevtsev (ed.), *Geological Composition of Krivoi Rog basin Iron Ores* [in Russian], Gosgeolizdat (1957).
9. Yu. G. Gershoig and E. Ya. Kaplun, "Ancient weathering horizon of metamorphosed magma rocks in the Krivoi Rog," *Dokl. Akad. Nauk SSSR*, 195, No. 4, 915-918 (1970).
10. Yu. G. Gershoig, and E. Ya. Kaplun, "Ancient weathering horizon of the Saksagansk granites Krivoi Rog," *Weathering Horizons* [in Russian], No. 12, Nauka, Moscow 91-110, (1973).
11. V. K. Golovenok, "Precambrian horizons of chemical weathering, their characteristics and the method of lithological-geochemical study," in: *Precambrian Weathering Horizons* [in Russian], A. V. Sidorenko, (ed.), VIMS, Moscow (1975), pp. 16-27.
12. M. Gorai, *Evolution of the Expanding Earth* [in Russian], Nedra, Moscow (1984).
13. P. K. Dement'ev, A. I. Bezgubov, and I. S. Modnikov, "Lower Proterozoic weathering horizons of the southern Russian Platform," *Sov. Geol.*, No. 8, 60-73 (1974).
14. M. N. Dobrokhotov, "The question of the stratigraphy of the early Precambrian of the Middle Dnepr region," *Geol. Zh.*, 24, 85-93 (1964).
15. A. D. Dodatko, "New data on the early Proterozoic metamorphosed weathering horizons of the Krivoi Rog-Kremenchugsk metallogenic zone of the Ukrainian Shield," *Geol. Zh.*, 44, No. 5, 8-13 (1984).
16. A. D. Dodatko, N. I. Kukhareva, and E. A. Semergeeva, "New data on the ancient metamorphosed weathering horizon of igneous rocks of the Saksagansk region of the Krivoi Rog basin," *Izv. Akad. Nauk SSSR, Ser. Geol.*, No. 5, 126-137 (1972).
17. A. D. Dodatko, N. I. Kukhareva and E. A. Semergeeva, "Metamorphosed weathering horizon on amphibolites of the Krivoi Rog Series," *Litol. Polezn. Iskop.*, No. 3, 44-45 (1975).
18. *Precambrian Iron-Silica Formations of the European Part of the USSR. Formation Types* [in Russian], Naukova Dumka, Kiev (1988).
19. N. P. Semenenko (ed.), *Precambrian Iron-silica Formations of the Ukrainian Shield* [in Russian], Naukova Dumka, Kiev, Vols. 1 and 2 (1978).

20. V. M. Zinchenko, "Pre-Krivoi Rog metamorphosed weathered horizon metabasites in the area of the Zheltorechensk structure (northern Krivoi Rog basin)," *Geol Zh.*, 41, No. 5, 150-154 (1981).
21. E. Ya. Kaplun, "Proterozoic metamorphosed weathering horizon of plagioclase granites under talc schists in the Krivoi Rog basin," *Dokl. Akad. Nauk*, 206, No. 2, 440-443 (1972).
22. E. Ya. Kaplun, "Age relationships of Precambrian rocks of the Saksagansk region, Krivoi Rog basin, and the study of the oldest metamorphosed weathering horizons," *Dokl. Akad. Nauk SSSR*, 209, No. 6, 1395-1397 (1973).
23. G. Kukla, *Rate of Geological Processes* [Russian translation], Mir, Moscow (1987).
24. M. P. Kuleshov, *Rock Age Interrelationships in the Krivoi Rog Region*, [in Russian], Gosgeoltekhizdat, Moscow (1957), pp. 24-41.
25. D. A. Kulik, *Formation conditions of banded iron quartzite structures in the Krivoi Rog basin Formation* [in Russian], Preprint IGFM, Akad. Nauk Ukr. SSR, (1986).
26. D. A. Kulik, "Types and genesis of the banded iron quartzite structures in the Saksagansk Formation, Krivoi Rog basin," *Candidate dissert.*, Geol.-Min. Sciences, IGOM, Academy of Sciences of the Ukrainian SSR, Kiev (1986).
27. E. A. Kulish, V. V. Pokalyuk and V. V. Reshetnyak, "Mineralogical-geochemical characteristics of the Upper Archean weathering horizons of Krivoi Rog," *Zap. Vses. Mineral. O-va*, 116, No. 5, 564-573 (1987).
28. N. I. Kukhareva, "New data on the contact between amphibolites and granites in the Saksagansk area," *Geol. Zh.*, 32, No. 1, 56-64 (1972).
29. Yu. P. Mel'nik, *Physicochemical Formation Conditions of Precambrian Iron Quartzites* [in Russian], Naukova Dumka, Kiev (1973).
30. Yu. P. Mel'nik, *Genesis of Precambrian Banded Iron Formations* [in Russian], Naukova Dumka, Kiev (1986).
31. E. K. Lazarenko, (ed.), *Mineralogy of the Krivoi Rog basin* [in Russian], Naukova Dumka, Kiev (1977).
32. B. M. Mikhailov and T. S. Petrovskaya, *Lithology of Mesozoic and Cenozoic Deposits of the Turg basin* [in Russian], *Trudy VSEGEI, New Series*, 24, (1959).
33. B. M. Mitsyuk and L. I. Gorogotskaya, *Physicochemical Alternation of Silica During Metamorphism* [in Russian], Naukova Dumka, Kiev (1980).
34. A. S. Monin and O. G. Sorokhtin, *Evolution of oceans and geochemistry of continental evolution*, *Vestn. Akad. Nauk SSSR*, No. 6, 99-110 (1983).
35. V. P. Petrov, *Introduction to the Study of Ancient Weathering Horizons* [in Russian], Nedra, Moscow (1967).
36. N. A. Plaksenko, *Basic Principles of Precambrian Iron Ore Sediment Accumulation* [in Russian], *Izd. Voronezh Univ.*, Voronezh (1966).
37. Yu. Ir. Polovinkina, "Stratigraphy, magmatism and tectonics of the Ukrainian Shield in the Precambrian," *Tr. Lab. Precambr. Geol.*, No. 2, 44-77 (1953).
38. Yu. A. Rus'ko, *Kaolinitization and Kaolins of the Ukrainian Shield* [in Russian], Naukova Dumka, Kiev (1976).
39. N. P. Semenenko, N. I. Polovko, G. V. Zhukov and others, *Petrography of Iron-silicate Formations of the Ukrainian Shield* [in Russian], *Izd. Akad. Nauk UkrSSR* (1956).
40. N. M. Strakhov, *Lithogenetic Types and Their Evolution Through Earth History* [in Russian], Gosgeoltekhizdat, Moscow (1963).
41. L. Ya. Khodyush, "Banded structure of iron quartzites and its origins," *Formation Problems of Precambrian Iron Rocks* [in Russian], Naukova Dumka, Kiev (1969), pp. 242-258.
42. N. P. Shcherbak, K. E. Esipchuk, B. Z. Berzenin, and others, *Precambrian Stratigraphic Sections of the Ukrainian Shield* [in Russian], Naukova Dumka, Kiev (1985).
43. H. D. Holland, *The Chemical Evolution of Atmosphere and Oceans*, Princeton (1984).
44. A. F. Trendall (ed.), *Iron-formation: fact and problems*, Elsevier, Amsterdam (1983).
45. A. F. Trendall and J. G. Blockley, "The iron formations of the Precambrian Hamersley Group, Western Australia, with special reference to the associated crocidolite," *Bull. West Austral. Geol. Surv.*, 119 (1970).

ISOTOPIC COMPOSITION AND ORIGIN OF CARBONATE MANGANESE ORES OF THE MANGYSHLAK DEPOSIT

V. N. Kuleshov and Zh. V. Dombrovskaya

UDC 550.4:553.32(574.1)

We found a broad spectrum of variations in isotope ratios in a study of the isotope compositions of the carbon and oxygen within various types of carbonate matter (carbonate manganese ores, calcite concretions, disseminated carbonate cement, etc.) occurring within the Mangyshlak deposit. Based on the patterns of distribution of the carbonate manganese ores, we concluded that they formed during the diagenesis stage, with the active participation of organic matter, and that the secondary segregations of carbonates (calcite) have a catagenic origin.

Geological Position, Depositional Environment, and Types of Manganese Ores

The Mangyshlak manganese deposit is located in Western Kazakhstan (Eastern Prikaspii) on the southern slope of the Kara Tau Ridge and, from a structural point of view, belongs to the northern border of the Chakyrkansky syncline joined with the Kara Tau anticlinorium.

Predominantly Cenozoic deposits are involved in the geological structure of the region. The manganese ores are associated with Oligocene sediments approximately 80 m thick in the region of the deposits. Three packets can be distinguished within their section (bottom to top): 1) blue-gray sandy marls; 2) gray and bluish-gray sands and siltstones with an orebearing horizon at the top; 3) gray, brownish-gray and brown clays with inclusions of limonite and gypsum [1]. Their respective names are: the Uzunbassk (Lower Oligocene), Kyulussk, and Kendzhalinsk (Middle Oligocene) suites [19]. The rocks of the Kendzhalinsk and Kyulussk suites are partially altered by weathering within the area of the deposit. Above, they are transgressively overlapped by Middle and Upper Miocene and Pleistocene deposits with a total thickness of approximately 100 m. The northern portion of the deposit was eliminated by erosion. A pinching out of the ore body occurs to the southwest. In many places, the ore body is exposed by deep ravines (Fig. 1).

The sediments of the ore-enclosing Kyulussk suite are represented by gray, unconsolidated, sandy-silty rocks over the entire area of the deposit, with the exception of the pinch-out area. Detrital material constitutes up to 70% of the volume of rock here, the material is angular and almost unrounded. All of the evidence suggests its arrival from nearby land which, during Kyulussk times, was represented by islands extending in a northwestern direction [25]. The detrital grains are represented primarily by feldspars (40-55%), quartz (30-45%), and fragments of various rocks (10-15%). Among authigenic minerals, there is a significant quantity (10-15%) of glauconite. The clayey cement is composed of montmorillonite.

In pinch-out regions the rocks of the Kyulussk suite are represented by dense carbonate clayey siltstones and marls with bluish-gray color and signs of having been slightly baked. In the direction in which the ore body pinches out, the quantity of detrital material and the grain-sizes of such material decrease, while the content of clayey-carbonate cement increases.

An ore stratum up to 20 m thick coincides with the Kyulussk suite, where it is represented by a series of several (up to 12) ore layers lying in the midst of country rock (Fig. 2). The ore matter is present in the form of individual nodules from 5 to 60 cm in size. These often occur in a single series within a layer and in the form of earthy masses sometimes forming beds up to 1 m thick and containing separate nodules. The ore matter plays the role

Geological Institute, Academy of Sciences of the USSR, Moscow. Translated from *Litologiya i Poleznye Iskopaemye*, No. 2, pp. 50-62, March-April, 1990. Original article submitted January 26, 1989.

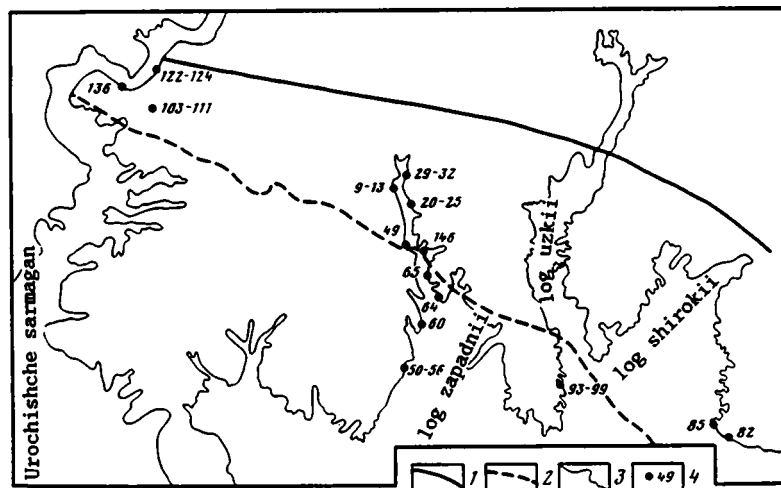


Fig. 1. Map of locations of samples collected for isotope analysis. 1) northern boundary of recent occurrence of manganese ores; 2) southern distribution boundary of oxide concretions; 3) contours of ravines revealing Oligocene deposits with manganese concretions; 4) sites where samples were collected.

of a basal cement in the enclosing sandy-silty rocks. Within the boundaries of this deposit pinch-out of the productive horizon occurs very abruptly and rapidly (over a distance of 100-300 m): the number of ore beds drops to 1-2 and the sizes of the nodules decrease from the sizes indicated to several millimeters.

The manganese ores in the Mangyshlak deposit are represented by carbonates, Mn oxides and mixtures of the two. Correspondingly, one can distinguish carbonate, oxide, and oxide-carbonate types of manganese ores. The oxide-carbonate and oxide types of ores arose, as pointed out by A. G. Betekhtin [3] and then N. M. Strakhov [20], as a result of hypergene oxidation of carbonate ores. They occur in the uplifted northwestern portion of the deposit and along ravines exposing the ore body.

The carbonate ores are represented by dense nodules confined to the sandy-silty and clayey-silty-carbonate cement of the enclosing rocks. The nodules are similar in color to the enclosing rock. They are grayish, and are distinguishable from the enclosing rock by their high density. The carbonate ores are characterized by variable compositions of their components, in particular, the ratios of MnCO_3 to CaCO_3 span a broad range. FeCO_3 and MgCO_3 are practically absent. According to the data of E. S. Tikhomirov and E. V. Cherkasov [21, 22], the carbonate ores are composed of calcic rhodochrosite with an admixture of manganocalcite and calcite. At the pinch-out of the ore horizon, the ores are composed of manganous calcite with an admixture of manganocalcite and relicts of calcic rhodochrosite. In this case, the value of $\text{MnCO}_3/\text{CaCO}_3$ decreases from 1.3-4.4 to 0.19. There is a complete absence of ferruginous carbonates within the ore packet.

The almost complete absence of organic matter within the carbonate ores and the enclosing terrigenous rocks of the productive horizon (in the presence of numerous impressions of such organic matter) is evidence of past diagenetic processes.

As a rule, several concretionary beds represented by calcite and containing almost no Mn carbonates are found at a stratigraphically lower level than the beds of manganese-ore concretions (see Fig. 2). In the oxidized varieties within these layers, there are small (4-6%) quantities of Mn oxides in the form of black, fused concentrates. The calcite nodules differ in size and shape from the manganese-ore concretions: they have simpler bun-or-biscuit-like shapes and, as a rule, are larger, reaching lengths of 1 m and more. Their surfaces are even and smooth. Their differences suggest different conditions associated with the formation of the upper and lower portions of the concretionary section.

In addition to the concretionary and primarily disseminated carbonate accumulation within the ore stratum, secondary calcitization occurs ubiquitously. It occurs in the presence of aggregates of crystalline calcite within the cement of the rock enclosing the ore concretions and also within the cavities of oxidized manganese concretions. The quantity of calcite usually amounts to several percent, reaching 20% in individual areas. More intensive (40-50%) calcitization occurs only in the northwestern portion of the deposit, where the rocks of the ore horizon are overlapped

by conglomerates of the Tortonian in the Miocene. The overlapping conglomerates are also cemented with crystalline calcite; this indicates a post-Tortonian process of superimposed calcitization.

Characterization of the Samples Studied

Isotopic investigations were carried out on the rock material collected within areas of Sartagan and Chakyrkan, predominantly within sections exposed by ravines and partially from core from bore holes. The locations of the samples studied over the area of the deposit and within the vertical section are shown in Figs. 1 and 2. The isotopic determinations were preceded by a detailed study of more than 200 samples in thin sections and heavy concentrates, clarification of the structural-textural peculiarities and paragenetic mineral associations of the samples, and a mineralogical investigation of the samples using chemical, spectral, thermal, x-ray, and other forms of analysis.

For the isotopic investigations, we selected rock material (36 samples) characterizing all of the genetic and petrographic varieties of carbonate formations from the Mangyshlak productive manganese stratum. Five groups were distinguished among these varieties: 1) carbonate, partially oxidized manganese-ore concretions and carbonate nuclei from oxide-carbonate concretions occurring in the oxidized portion of the deposit; 2) carbonate nodules and loose carbonate containing material from the rocks of the Kyulussk suite at the western pinch-out of the ore horizon; 3) secondary carbonate from the enclosing ore concretions of the sandy-silty rock within the central portion of the deposit; 4) calcite concretions from the lower portion of the concretionary section; 5) carbonate enclosing and cementing oxidized ores in the northwestern portion of the deposit. In addition, the carbonate rocks from the underlying ore stratum (limestone, P_2^{ad} , Sample 13-1) and overlapping, younger rocks (carbonate cement of the supra-ore conglomerate, $N_1^{kr} + kn$, Sample 103) were analyzed for comparison.

First Group. The carbonate manganese-ore nodules are partially oxidized over an appreciable area of their occurrence. The oxidized layer is situated on the outside of the concretions, is clearly expressed, and has a thickness from several millimeters to 2 cm. A carbonate nucleus containing a variable quantity of manganese oxides is preserved within. The carbonate material is composed of cryptocrystalline aggregates cementing a sandy-silty mixture. According to calculations from the chemical analyses of Samples 49, 93, 94, 95, 96, the amount of the non-carbonate mixture amounts to 58.53-76.75%. The content of $MnCO_3$ varies from 6.89 to 41.47%, the content $CaCO_3$ varies from 1.79 to 19.69%. $MnCO_3$ is present in two of the samples in quantities of 1.05-1.32%; $FeCO_3$ is absent.

There is a clearly expressed endoeffect in the region of 600°C on the heating curves. This indicates a rhodochrosite composition for the material. There are sometimes additional endoeffects in the region of 600-850°C suggesting an admixture of calcium-containing carbonates. On x-ray diffraction patterns, one can see intensive reflections of rhodochrosite $d_{1014} = 2.85 \text{ \AA}$ and also a low-intensity value for d_{1014} equalling 2.90-3.01 Å, indicating an admixture of mixed Mn-Ca carbonates. The investigations thus show that the carbonate matter in the manganese-ore concretions is represented by rhodochrosite or a mixture of rhodochrosite with intermediate members of the rhodochrosite-calcite isomorphic series.

The unconsolidated sandy-silty matter within the oxide concretions of the geode type [15] forming during an almost complete disintegration of the carbonate material (Sample 29-32), contains small (~3%) quantities of carbonates, where $MnCO_3$ amounts to approximately ~1% and $CaCO_3$ equals ~2%. According to the data of the x-ray diffraction analysis, the carbonates are represented by manganoclacite with a $MnCO_3$ content ranging from 20 to 50%. Significant (9-11%) quantities of manganapatite are contained in the leached nuclei, according to the data of the x-ray diffraction analysis and calculations from the chemical analyses.

Second Group. The ore matter occurring at the western pinch-out of the ore body is represented by small carbonate nodules and unconsolidated carbonate material disseminated within a clayey-silty mass. The carbonate matter is cryptocrystalline. Its distribution within the rock is uneven, often forming coagulates and areas transitional to nodules. According to the data from the calculations in the chemical analyses (Sample 14-5), the carbonate matter in the nodules constitutes 80-90% of the total. As a rule, $MnCO_3$ predominates over $CaCO_3$ within this carbonate matter, although not to a great extent. According to x-ray diffraction data (Sample 14-5), the carbonate matter is represented by a mixture of rhodochrosite and manganocalcite with a $MnCO_3$ content ranging from 20 to 50%. The unconsolidated carbonate matter is most often composed of calcite (Samples 14-4, 17-8), but manganocalcite with a $MnCO_3$ content of 50% (Sample 14-6) and rhodochrosite (Sample 17-4) are also encountered.

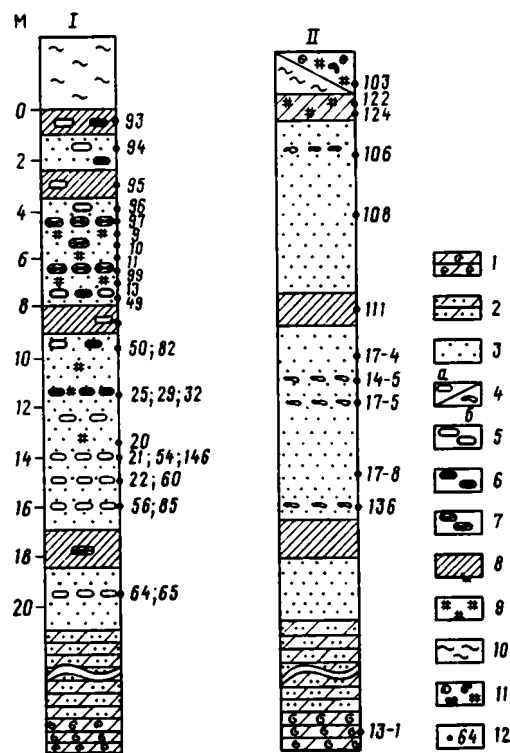


Fig. 2. Typical composite geological columns of the manganese-bearing beds of the Mangyshlak deposit. I) Within the area of the deposit; II) at the pinch-out of the ore body. 1) White and rose limestones, organogenic, small-scale Adaevsk suite (P_2^3ad); 2) blue-gray marl, sandy Uzunbassk suite (P_3^1us); 3-9) ore-bearing horizon, Kyyuluskk suite (P_3^2kl): 3) sandy-silty deposits, gray and bluish-gray; 4) carbonate nodules (a: predominantly calcite, b: small nodules); 5) oxide-carbonate nodules; 6) oxide nodules of the geode type, 7) ferruginous oxide nodules; 8) bedded earthy manganese ores; 9) superimposed calcitization; 10, 11) overlapping rocks: 10) brownish-gray and brown limonized and gypsumized, Kendzhalinsk suite ($P_3^2 kn$); 11) conglomerate in calcareous cement with fragments of oxide Mn-ore, Tortonian stage, Konsk and Kragansk horizons ($N_1^2 kn + kr$); 12) sample selection site and its number.

Third Group. Carbonate plays an insignificant role in the rocks enclosing the oxidized ore concretions. As a result of weathering, the initial unconsolidated manganese-bearing carbonates here are oxidized and can be identified by black, sooty appearance. The enclosing rocks have high effective porosities in such cases. Secondary carbonates in the form of coarse-grained aggregates cement small areas of the enclosing rocks and infill leached cavities in the oxidized concretions. The calculations from the chemical analyses of the enclosing rocks (Samples 9, 11, 13) indicate that the carbonate content within these rocks amounts to 4.41-7.96%, with the predominant portion belonging to $CaCO_3$ and no more than 1% belonging to $MnCO_3$.

Fourth Group. The carbonate concretions lying within the lower portion of the concretionary section are composed of cryptocrystalline aggregates. According to the calculations from the chemical analyses (Samples 10, 21, 22, 65), the carbonate content amounts to 20.61-28.49%; the remaining portion of the aggregates belongs to a terrigenous admixture. $CaCO_3$ sharply predominates within the composition of the carbonates (18.12-28.49%). The content of $MnCO_3$ is usually less than 1%. In contrast to the manganese-ore concretions, there are small (1.08-2.01%) quantities of $FeCO_3$ here. On the heating curves (samples 10, 21, 22, 54, 60, 64, 65), there are broad, asymmetrical endoeffects within the 600-850°C region, with deep troughs at 800°C suggesting a calcite component within the rock. The asymmetry of the left limb of the curve suggests an admixture of manganese-bearing carbonates within the

sample. On the x-ray diffraction patterns of the samples, the reflection $d_{10\bar{1}4} = 3.019 \text{ \AA}$ with an intensity of 10 indicates a calcite composition for the carbonate.

Fifth Group. The carbonate cementing the oxidized, water-worn ores at the contact with the overlapping Middle Miocene sediments (the Tortonian) occurs in the form of a solid cryptocrystalline cement with oxidized ores preserved in irregularly shaped areas within it. The carbonate content, according to the data of calculations from the chemical analyses (samples 122, 124), equals 32.28–45.33%; this material is CaCO_3 for the most part. In Sample 122, we determined $\text{MgCO}_3 = 2.37\%$, while $\text{MnCO}_3 = 1.85\%$ in Sample 124. On the heat curves, there are broad endoeffects within 600–850°C region, with a maximum at 800°C, indicating a calcite component in the sample. The asymmetry of the left limb of the effect is due to an admixture of manganese-bearing carbonates.

The overlapping ore horizon of Middle Miocene conglomerates is cemented by cryptocrystalline calcite (Sample 103) similar to that described above. Among the lumps of various composition, the conglomerates contain fragments from concretions of oxidized carbonate ores.

The material for the isotopic investigations was collected within areas of Sartagan and Chakyrghan, predominantly in sections exposed by ravines. The positions of the samples studied within the vertical section and over the area are shown in Figs. 1 and 2.

Methodology of the Experiment

The standard methodology involving decomposition of the carbonates in orthophosphoric acid (H_3PO_4) at room temperature was primarily used in the preparation of samples for mass-spectral analysis [29]. However, in connection with the fact that the samples studied possess different mineral compositions of carbonates (the isomorphic series: calcite-manganocalcite-rhodochrosite) and, consequently, different rates of solution in acid, we settled upon using a stepwise breakdown of the samples [26, 30]. In this process, it was assumed that the first portion of CO_2 gas liberated during the first 1–1.5 h corresponds to a decomposition production of calcite and that the isotopic ratio measured in this gas corresponds to the isotopic composition of the decomposed calcite. During breakdown of carbonates which were difficult to dissolve, the sample was kept in a reactor to prolong decomposition for 1–2 days. It was assumed accordingly that the second portion of gas collected corresponded to the decomposition product of the rhodochrosite, Ca-rhodochrosite and manganocalcite.

Naturally, such a methodological approach, based upon the different rates of solution for the different carbonate minerals in the acid, can involve well-known methodological errors. Nonetheless, this technique is very useful for solving the problem presented before us.

For a small portion of the samples, we used, in addition to the methodology described above, a methodology for decomposing carbonates in a melt of lead chloride (PbCl_2) as proposed by Yu. A. Borshchevskii et al. [14]. In this case, a weight (20 mg) of pre-dissolved sample was taken and carefully mixed with the reagent (PbCl_2) for an experiment. The sample prepared in this fashion was poured into a container made of nickel foil and heated in a reactor where it was pumped to a forevacuum. The reaction was carried out at a temperature of 550–600°C for 20 min.

The measurement of carbon and oxygen isotopic compositions were carried out on a MI-1201B mass spectrometer of domestic manufacture. The measurement error in parallel experiments involving oxidative decomposition of the sample equaled $\pm 0.25\%$; the error equaled $\pm 0.5\%$ for decomposition within the PbCl_2 melt.

Isotopic Data and Their Discussion

All of the results of the isotopic investigations are presented in Table 1 and shown on a graph (Fig. 3). From these presentations, it follows that the total scatter of values for the isotopic composition spans a broad range from -32.9‰ to $+1.4\text{‰}$ for $\delta^{13}\text{C}$ and from 15.8 to 30.9‰ for $\delta^{18}\text{O}$, i.e., the total scatter of values overlaps the region of isotopic indices characteristic to the polar groups of the carbonaceous matter in the earth's crust: sedimentary marine carbonates and carbon of organic origin. At the same time, the separate groups of material studied are characterized by surprisingly constant isotopic compositions, despite the broad range of variation in isotopic ratios mentioned.

TABLE 1. Isotopic Compositions of Carbon and Oxygen within the Rocks of the Mangyshlak Manganese Deposit

Analysis No.	Sample No.	Characterization of sample	$\delta^{13}\text{C}, \text{‰}$ (PDB)	$\delta^{18}\text{O}, \text{‰}$ (SMOW)
Manganese-ore concretions and carbonate nuclei from zonal oxide-carbonate concretions				
1884	49	Carbonate nucleus (rhodochrosite)	-19.0	29.6
1999	50	Same	-32.9	30.9
2002	93	Carbonate nucleus (calcite)	-1.9	15.8
		Same (rhodochrosite)	-16.2	26.0
2611	94	"(calcite)	-9.1	22.6
		"(rhodochrosite)	-11.9	22.0
2003	96	Same	-20.5	29.4
1993	29	Weathered nucleus (calcite)	-8.7	19.8
1995	32	Same	-7.8	27.8
2611	146	Carbonate (Mn-Ca) concretion	-10.1	19.0
2612	95	Same (calcite)	-5.6	18.9
		"(rhodochrosite)	-6.9	27.4
Carbonate formations at pinch-out of ore body				
2616	106	Carbonate nodules (calcite)	-4.2	26.5
		Same (rhodochrosite)	-4.7	28.4
2617	108	Carbonate concretions (calcite)	-8.4	27.4
		Same (rhodochrosite)	-8.8	30.6
2618	111	"(calcite)	-9.9	27.9
		"(rhodochrosite)	-14.5	27.6
2008	14-5	Carbonate (Mn-Ca) nodules	-7.5	28.8
2009	17-4		-9.7	23.7
2624a	17-5	Siltstone with carbonate cement	-0.8	27.6
26246	17-8	Silty marl	0	27.1
2620	136	Carbonate nodules (calcite)	-4.4	19.3
Calcite from cement of rock enclosing oxidized concretions				
2596	9	Siltstone with calcite (4%) in cement	-5.5	18.4
2598	11	Same (8%)	-6.8	16.9
2599	13	(7%)	-5.8	17.9
2600	20	Siltstone with calcite in cement	-5.7	19.0
2603	25	Same	-6.4	18.0
Calcite concretions from lower portion of section				
2597	10	Calcite concretion with 6% Mn oxides	-5.6	18.9
2601	21	Same	-5.4	19.3
2602	22	"	-5.2	19.0
2604	54	" (CaCO ₃ , 35%)	-3.0	22.6
2605	56	"	-3.9	19.6
2606	60	" (CaCO ₃ , 40%)	-5.9	18.8
2607	64	" (CaCO ₃ , 30%)	-6.9	16.5
2608	65	" (CaCO ₃ , 28%)	-7.9	20.1
2610	85	"	-7.0	17.7
2614	99	"	-6.9	19.4
Carbonate from oxidized ore of northwestern area of deposit				
2619	122	Calcite cement of manganesian rock	-4.4	18.7
2005	124	Same	-4.0	20.3
2615	103	Calcite from cement of supra-ore conglomerates	-4.3	20.8
2623	13-1	Upper Eocene organogenic limestone	+1.4	27.9

The carbonate material of the marls enclosing the ore nodules (Sample 17-8) and clayey-carbonate siltstones (Sample 17-5) in the region of the western pinch-out of the ore stratum of the deposit are characterized by carbon and oxygen isotopic ratios characteristic of marine carbonates of normal sedimentary origin (See Fig. 3, region A), as is the case with the underlying Upper Eocene limestones (Sample 13-1). It is necessary to note, that all of the other analyzed

varieties of carbonate formations are characterized by isotopic compositions different from those of marine carbonates.

These isotopic data allow us to formulate conclusions concerning the formation of the indicated disseminated carbonates within regions where the ore body pinches out in the normal sedimentary fashion and to attribute primary materials to such pinch-outs.

A characteristic feature in the distribution of the isotopic data on the carbonate ores is the fact that all of the ores are distinguished by significant scatters of $\delta^{13}\text{C}$ values: from -32.9 to -4.7‰ . The isotopic composition of the oxygen within the ores remains fairly constant in this situation; values of $\delta^{18}\text{O}$ vary from 27.6 to 30.9‰ .

The broad scatter in values of $\delta^{13}\text{C}$ observed in the ores suggests that the system in which the formation of the manganese carbonates occurred was not homogenous with respect to carbon and was at disequilibrium with regard to the isotopic ratio. The lowest values turn out to be analogous to those for carbon of organic origin [10]. At the same time, a portion of the samples with high $\delta^{13}\text{C}$ values adjoin a region characteristic of marine sedimentary carbonates (see Fig. 3, region A). This fact suggests that the carbon dioxide in the carbonate ores had a heterogeneous origin and represents a composite line due to substances from two sources. Carbon dioxide of organic origin, characterized by isotopically light carbon, serves as one of these substances. It is formed in the zone of diagenesis in the upper layers of muddy sediment as a result of the oxidation of organic matter. The other, isotopically heavy substance is CO_2 derived from marine sedimentary carbonates.

The high values observed for the isotopic composition of the oxygen in the carbonate manganese ores and the narrow range of variations in such values suggests isotopic-equilibrium conditions with sea water when carbonate formation took place at low temperatures [27].

The isotopic data obtained and the patterns of their distribution thus suggest the formation of the carbonate manganese concretions of the Mangyshlak deposit under diagenesis conditions (see Fig. 3, region B).

The conclusion obtained and the experimental data for the Mangyshlak deposit are in good agreement with the isotopic data for the manganese ores of other deposits [11, 13].

The following pattern can be detected against a background of broad variations in isotopic ratios within manganese ores. The pattern consists in the fact that only the carbonate concretions of the zone of western pinch-out occupy the region of the highest $\delta^{13}\text{C}$ values. At the same time, the oxide-carbonate zonal concretions in the central areas of the deposits coincide with a region of low $\delta^{13}\text{C}$ values. This fact indicates certain geochemical differences associated with the formation of these concretions. It can be assumed that the weighing of the isotopic composition of the carbon in the carbonate manganese concretions found in the zone of western pinch-out is connected with the higher overall carbonate content of the terrigenous-clayey sediment enclosing the nodules and the minor participation of organics during the diagenesis process. On the other hand, in the lateral zone of the sedimentary paleobasin closer to the shore, where predominantly oxide-carbonate ores occur, the original carbonate content of the sediment (at the moment of sedimentation) is insignificant. The activity of the organic matter was much higher during the diagenesis process in this zone. All of this is reflected in the observed correlational dependence between the isotopic composition of the carbon and of the manganese contents in the ores (Fig. 4). It is therefore precisely within the portion of the productive packet's lateral profile closer to the shore, where the diagenesis processes proceeded most intensively, that we find the maximum volumes of ore material.

The calcites from the cement of the enclosing rocks in the ore-bearing horizon and the calcite concretions turn out to be different in isotopic composition from the groups of manganese-ore carbonates in the deposits discussed above. These calcites are characterized by a fairly narrow range of variations in isotopic ratios and form a separate region C on the graph (see Fig. 3). In contrast to sedimentary carbonates of marine origin, they are generally characterized by lighter isotopic compositions of the carbon ($\delta^{13}\text{C} = -8\text{‰} \dots -2\text{‰}$) and oxygen ($\delta^{18}\text{O} = 16\text{‰} \dots 22\text{‰}$). They differ from diagenetic carbonates in having lower $\delta^{18}\text{O}$ values.

Such isotopic ratios are generally characteristic of hydrothermal and catagenetic carbonates. However, the material composition, depositional environment, and other geological data on the deposit generally do not support a hydrothermal origin for the deposits.

It can be assumed on the basis of the existing isotopic data that carbon dioxide and water in solutions of the same origin participated in the formation of the carbonate cement and the calcite concretions.

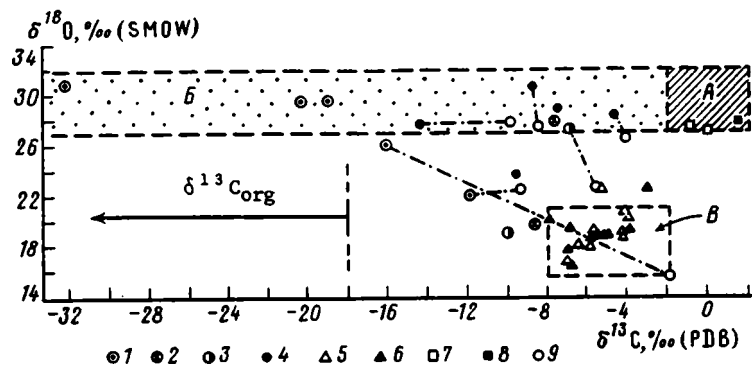


Fig. 3. $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ in carbonate rocks and ores of the Mangyshlak manganese deposit. Regions: 1) sedimentary marine sediments; B) diagenetic carbonates; C) catagenetic carbonates; 1, 2) carbonate and loose nuclei or oxide-carbonate concretions respectively, 3) massive oxide-carbonate concretions; 4) carbonate concretions of the pinch-out zone; 5) calcite from cement of enclosing rocks; 6) calcite concretions; 7) carbonate from country rock of the pinch-out zone; 8) underlying limestone; 9) calcite from rocks analyzed. Dashed line connects points corresponding to isotopic analyses for a single sample with respect to calcite and rhodochrosite.

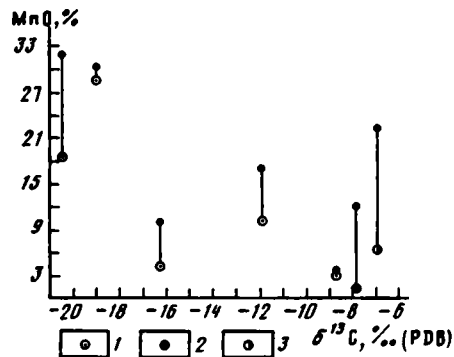


Fig. 4. Relationship between the isotopic composition of carbon and the MnO content in carbonate and oxide-carbonate ores. 1, 2) carbonate and loose nuclei of oxide-carbonate concretions respectively; 3) massive oxide-carbonate concretions.

It is impossible to say anything definite concerning the type of catagenesis [23, 24] and, naturally, the isotopic composition of the oxygen in the water participating in this process on the basis of the isotopic data. If it is assumed that these waters have isotopic compositions similar to the composition of the oxygen in sea water ($\delta^{18}\text{O} \sim 0$), then, keeping in mind the isotopic equilibrium of the process, carbonate precipitation should have taken place at high (80–120°C) temperatures. Geological data does not support this conclusion.

At the same time, if the formation of the carbonates took place with the participation of meteoric waters ($\delta^{18}\text{O} = -7 \dots -6\text{‰}$), the temperatures of carbonate precipitation for the major portion of samples studied should have equaled to 40–50°C in this case, although the total temperature interval could have been wider (30–70°C). Such temperatures are quite realistic and do not contradict geological observations.

An analogous distribution of carbon and oxygen isotopes occurs in cases when the formation of catagenetic carbonates originated from waters of an elisional origin. In general, elisional waters should be characterized by high concentrations of the light ^{16}O isotope in comparison with sea waters [28], and the $\delta^{18}\text{O}$ values could correspond to waters of a meteoric origin. On the basis of isotopic data alone, therefore, it is impossible to reliably establish the origin of the waters in the solutions (elisional or meteoric) which participate in the process of calcitization. A solution to this problem could be arrived at with additional (isotopic and geochemical) data in combination with geological data.

The isotopic data obtained indicate that processes of catagenetic carbonate formation proceeded intensively with the Mangyshlak manganese deposit. Neogenetic calcite was "nourished," apparently along with diagenetic ore carbonates, i.e., these enter into the composition of the manganese ores. The ratio of original diagenetic and catagenetic carbonates can vary over quite different values.

The addition of catagenetic calcite to the composition of the carbonate ores affected the isotope composition of the latter. This is beautifully illustrated by the graph in Fig. 3. It is evident on the graph that all of the calcites are shifted toward the side of lighter amounts of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ on the basis of isotopic characteristics, i.e., they all approach the region of catagenetic carbonates (region C). Their addition to the oxide-carbonate zonal manganese ores is responsible for the observed linear distribution of isotopic ratios of carbon and oxygen within the coordinates of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$.

The Genesis of the Deposit

A. G. Betekhtin [3] and then N. M. Strakhov et al., [20] and other investigators [2, 17] established that the oxide ores of the Mangyshlak deposit are the product of hypergene oxidation of primary carbonate ores. The most detailed account of the gneiss of the deposit, treated as a sedimentary-diagenetic process, is given in [20]. In the opinion of N. M. Strakhov, manganese entered into the basin together with terrigenous material from regions of drift. Carbonate concretionary ores were formed as a result of diagenetic redistribution of the ore substance.

In recent years, two points of view differing from the above have emerged with regard to the source of the ore substance and the corresponding genesis of the deposit: M. M. Mstislavskii [14] and I. P. Druzhinin [7-9] have treated the deposit as hydrothermal-sedimentary; V. N. Kholodov [24], V. I. Dvorov and E. A. Sokolova [5, 6, 16, 18] proposed an elisional-catagenetic model of manganese-ore genesis. There are geological-geochemical data of one or another degree of validity leading some support for the hypotheses mentioned.

The results of the isotopic investigations we carried out on the carbonate rocks of the Mangyshlak deposit could not reveal the source of the manganese for the formation of the ores, however, they allow us to assert that the carbonate manganese concretions have a diagenetic origin, i.e., the formation of the concretionary manganese carbonates occurred predominantly during a stage of diagenesis in muddy sediment with the active participation of organic matter. The intensity of the diagenesis processes and, consequently, the intensity of ore formation varied within the deposit. These processes were most actively manifested near the shores of zones of the paleobasin, i.e., in the central and, especially, northeastern portions of the deposit. Here, the sizes and quantities of concretionary formations increased, the shapes of the formations became more complicated, and the thicknesses of the material increased during the process of manganese-ore carbonate formation.

The original carbonate content of the sediment apparently increased toward the side of the deeper-water portions of the paleobasin. A fade-out of C_{org} activity during the diagenetic processes occurred in this direction. All of this is reflected in the weighing of the isotopic composition of the carbon in the carbonate ores, in the decrease in manganese content and the increase in CaO within the carbonate manganese ores (see Fig. 4).

Thus, our data completely supports the hypothesis of N. M. Strakhov and his co-authors that the carbonate ores of the Mangyshlak deposit formed under conditions of diagenesis.

At the same time, a significant portion of the carbonate material present within the deposit has a later, catagenetic origin. This material was superimposed upon the already formed manganese ores. Such carbonates include: a) carbonates occurring within the enclosing sandy-silty rocks; b) carbonates composing the concretionary nodules in the lower portion of the ore horizon; c) carbonates from the cement of the upper water-worn portions of the ore body and also from the overlapping conglomerates. All of the carbonates are predominantly represented by calcite.

The process of superimposed calcitization upon the Mangyshlak deposit took place after the Early Miocene oxidation of the carbonate ores. A wealth of geological data and, most importantly, the fact that the oxidized manganese ores everywhere contain secondary calcite segregations are evidence of this. In the northern water-worn portion of the deposit, both the rocks of the ore horizon and the conglomerates overlapping them were subjected to calcitization. This suggests that the carbonate-forming solutions penetrated along weakened zones, including a zone of discordant contact of the Oligocene and Middle Miocene deposits, during post-Early Miocene times. This zone is highly permeable, since it is composed of siltstones and conglomerates overlapping them.

It is difficult to make inferences concerning the origin of the waters participating in the process of catagenesis (and consequently, inferences concerning the type of catagenesis involved) on the basis of isotopic data. As we pointed out above, these waters could have been either elisional waters or waters of meteoric origin.

* * *

The results of this study of the isotopic composition of the carbon and oxygen in the oxide-carbonate and carbonate manganese ores and also the investigation into the various types of carbonate formations occurring within the Mangyshlak deposit allow us to make the following conclusions.

1. The carbonate material occurring within the region of pinch-out of the Mangyshlak deposit in the form of cryptocrystalline aggregates disseminated within the enclosing rock is a primary natural-sedimentary marine formation.

2. The carbonate concretionary ores of manganese in the Mangyshlak deposit have a diagenetic origin. They formed from disseminated carbonate manganese material with the active participation of organic matter.

3. The processes of diagenesis within the deposit manifested unevenly. They proceeded most actively within the central and northeastern areas of the deposit. The greatest thickness of deposits of ore substance are recorded here. The activity of these processes was reflected also in the lightening of the isotopic composition of the carbon in the manganese ores.

4. More recent carbonates of catagenetic origin widely occur with the deposit. During this stage, formation of carbonate ores did not take place. Catagenetic processes within the deposit generally resulted in the washing out (leaching of Mn) of the original ores.

LITERATURE CITED

1. M. V. Bayarunas, "Lower Oligocene deposits of Mangyshlak," in: *Zap. Imp. S.-Petersburg Mineralog. o-va*, Ser. 2, Chap. 49 (1912).
2. M. E. Berdichevskaya and V. P. Rakhmanov, "Prospective discoveries of manganese ores on the Mangyshlak Peninsula," in: *Commercially Valuable Minerals in Sedimentary Strata* [in Russian], Nauka, Moscow (1981), pp. 157-168.
3. A. G. Betekhtin, *Commercial Manganese Ores of the USSR* [in Russian], Akad. Nauk SSSR, Moscow-Leningrad (1946).
4. Yu. A. Borshchevskii, S. A. Borisov, and N. K. Popova, "New method of releasing oxygen and carbon from carbonates and carbonate-silicate rocks for isotopic analysis," *Text of the Proceedings of the All-Union Symposium on Stable Isotopes and Geochemistry*, Moscow (1974).
5. V. I. Dvorov and E. A. Sokolova, "The origin of the Mangyshlak manganese deposit," *Geol. Pud. Mestorozhdenii*, 28, 1, 98-100 (1986).
6. V. I. Dvorov and E. A. Sokolova, "Geological-geochemical prerequisites for the formation of the manganese ores of the Mangyshlak deposit. Part 2," *Litol. Polezn. Iskop.*, No. 4, 28-47 (1987).
7. I. P. Druzhinin, "Facial control of the manganese mineralization of Mangyshlak and the cyclical type of section structure," in: *New Data on the Manganese Deposits of the USSR* [in Russian], Nauka, Moscow (1980), pp. 191-199.
8. I. P. Druzhinin, "Facies of the Lower Maikopsk manganese deposits of Mangyshlak," in: *Commercial Minerals in Sedimentary Strata* [in Russian], Nauka, Moscow (1981), pp. 183-204.
9. I. P. Druzhinin, "Posterior stage of deep faulting, the hydrothermal process, and a new type of sedimentary trap during the formation of the marine manganese ores of Mangyshlak," *Dokl. Akad. Nauk SSSR*, 289, 5, 1194-1198 (1986).
10. L. A. Kodina and É. M. Galimov, "The formation of the isotopic composition of the carbon in organic material of the 'humus' or 'sapropel' types in marine sediments," *Geokhimiya*, No. 11, 1742-1756 (1984).
11. V. N. Kuleshov, "The origin of the manganese carbonate ores in of Nikopol'sk and Bol'she-Tokmaks deposits (based upon the isotopic compositions the carbon and oxygen)," *Proceedings of the XI All-Union Symposium on the Geochemistry of Isotopes* [in Russian], Lenin Institute of Geochemistry and Analytical Chemistry (1986), pp. 210-212.

12. V. N. Kuleshov and Zh. V. Dombrovskaya, "Isotopic composition and conditions of formation of the Nikol'sk carbonate manganese ores," *Isotopic Geochemistry of the Ore-Formation Process* [in Russian], Nauka, Moscow (1988), pp. 233-258.
13. V. N. Kuleshova and L. E. Sherenberg, "Isotopic composition of Fe-Mn Concretions of Lake Krasnovo (Karel'sk neck)," *Izv. Akad. Nauk SSSR, Ser. Geol.*, No. 10, 92-104 (1988).
14. M. M. Mstislavskii, "Paleotectonic features associated with the localization of Oligocene manganese-ore deposits in the southern USSR," *Dokl. Akad. Nauk SSSR*, 260, 5, 1207-1212 (1981).
15. L. V. Pustovalov, "The origin of the Lepetsk and Tul'sk iron ores," *Tr. Vsesoyuz. Geologo-Raved. Ob'edinenie*, No. 285 (1933).
16. E. A. Sokolova and V. I. Dvorov, "Geological-geochemical prerequisites for the formation of manganese ores of the Mangyshlak deposit. Part 1," *Litol. Polezn. Iskop.*, No. 1, pp. 60-79 (1987).
17. E. A. Sokolova, Zh. V. Dombrovskaya, and E. B. Tronn, "Structural features and the formation of the Mangyshlak manganese deposits in Kazakhstan," in: *Manganese Ore Formation in the Territory of the USSR* [in Russian], Nauka, Moscow (1984), pp. 242-249.
18. E. A. Sokolova and A. I. Sharanov, "The geochemistry of the Oligocene deposits in the region of the Mangyshlak manganese deposit," *Litol. Polezn. Iskop.*, No. 1, 59-77 (1986).
19. A. S. Stolyarov, "New data on the stratigraphy of the Oligocene deposits of Southern Mangyshlak," *Byul. ONTI, Gosgeoltekhizdat, Moscow*, No. 3, 8-10 (1958).
20. N. M. Strakhov, L. E. Shterenberg, V. V. Kalinenko, and E. S. Tikhomirova, "The geochemistry of the sedimentary manganese-ore process," *Tr. Geol. Inst. Nauk, Akad. Nauk SSSR* (1968), No. 185.
21. E. S. Tikhomirova, "Paleogeography and geochemistry of the Lower Oligocene manganese deposits of Mangyshlak," *Litol. Polezn. Iskop.*, No. 1, 75-92 (1964).
22. E. S. Tikhomirova and E. V. Cherkasova, "The distribution of minor elements in the ores of the Mangyshlak deposit of manganese," in: *Manganese Deposits of the USSR*, Nauka, Moscow (1967), pp. 258-273.
23. V. N. Kolodova, "News concerning the identification of catagenesis. Part 1," *Litol. Polezn. Iskop.*, No. 3, pp. 3-21 (1982).
24. V. N. Kolodova, "News concerning the identification of catagenesis. Part 2," *Litol. Polezn. Iskop.*, No. 5, pp. 15-32 (1982).
25. A. L. Yanshin, "The Paleocene of Mangyshlak," *Byul. Mos. Obshchest. Ispit. Prirod.*, 25, 4, 3-42 (1950).
26. S. Epstein, D. F. Graf, and E. T. Degens, "Oxygen isotope studies on the origin of dolomites," *Isotope and Cosmic Chemistry*, North-Holland, Amsterdam (1964), pp. 164-180.
27. J. Friedman and J. R. O'Neil, "Compilation of stable isotope fractionation factors of geochemical interest," *U.S. Geol. Surv. Prof. Paper 440-KK*, U. S. Government Printing Office, Washington (1977).
28. M. J. Mott, J. R. Lawrence, and L. D. Kcidwin, "Elemental and stable isotope composition of pore waters and carbonate sediments from deep sea drilling project sites 501/504 and 505¹," *Initial Reports of the DSDP*, Vol. 69, Washington (1983), pp. 461-473.
29. J. M. McCrea, "On the isotopic chemistry of carbonates and paleotemperature scale," *J. Chem. Phys.*, 18, 6, 849-857 (1950).
30. H. J. Walters, J. G. E. Claypool, and Ch. With. Philip, "Reaction rates and ¹⁸O acid preparation method," *Geochim. Cosmochim. Acta*, 36, 2, 129-140 (1972).

CONDITIONS SURROUNDING THE FORMATION OF STRATIFORM ZEOLITE DEPOSITS

V. I. Gugushvili, Ts. Sh. Kargareteli, and K. I. Omiashvili

UDC 553.673

In the article, we show that the stratiform deposits of highly siliceous zeolites (clinoptilolite, and phillipsite) and the agate-chalcedonic deposits in the Eocene volcanic stratum of Meskhetiya formed under various geological conditions. Volcanogenic-exhalational zeolitization took place in a subaqueous environment and agate-chalcedonic mineralization of cavities took place in a subaerial environment. Subaerial conditions arose as a result of the bulging of volcanic ranges and islands above sea level. We reconstructed the dellenic ridge dividing the Eocene sea into basins with various types of sedimentation, essentially volcanic and tephroid. The volcanogenic-exhalational zeolitization was associated with the latter.

The most significant agate-chalcedonic and zeolite deposits in Georgia occur in the southern Adzhar-Trialetsk folded zone, in Meskhetiya, within the Akhaltsikhsk depression, and on the southern slope of the Adzhar-Imeretia Range (Fig. 1). These deposits are situated on the upper layers of a Middle Eocene volcanic stratum within the Kvabiskhevsk and Dvirsk suites (Fig. 2). Judging from the shapes of the deposits and the gravitation toward zones of crushing and argillization, the agate-chalcedonic occurrences are epigenetic formations relative to the enclosing dellenicites, whereas the tephroid occurrences were subjected to zeolitization simultaneously with their precipitation, a precipitation accompanied by the formation of stratiform zeolite deposits. The agate-chalcedonic and zeolite deposits of Meskhetiya were recently studied and the results were presented in numerous publications [1-8, 12-14]. Up until now, however, the question of geological conditions and paleogeographic environments of their formation have not been covered in such collections. Also, the genetic interrelationships associated with the deposits have not been studied. We have attempted to fill this gap.

Geological Structure of the Agate-Chalcedonic and Zeolite Deposits

Meskhetiya is composed of two sharply differing morphological units: the Adzhar-Imeretia Range in the north and the Akhaltsikhsk depression in the south. These units are separated by a deep fault outlining the subsidence of the depression (Fig. 1).

The ore-enclosing Middle Eocene stratum consists of an alternation of suites differing in composition and textural-structural features (Fig. 2). The lowest, the Likansk suite, is composed of layered tufts, tuffobreccias, and also lavas of a basaltic composition. The Kvabiskhevsk suite follows the Likansk suite. It consists exclusively of lavas and hyaloclastics arranged in homodromal sequence, from basalt and andesite-basalt to andesites, andesites-dacites, and dellenicites. The Dvirsk suite lies above the Kvabiskhevsk suite; it is represented by two facies: 1) coarsely fragmental, massive tuffobreccias of andesitic-basaltic composition and 2) an alternation of thin-layered and finely granular tufts of a tephroid appearance interstratified with marls and pelitomorphous limestones (the Gurkel'sk facies). Within the boundaries of the southern slope of the Adzhar-Imeretia Range, the Middle Eocene volcanic stratum outcrops over the entire thickness under conditions of deep erosional cutting, whereas, only the upper layers of the Kvabiskhevsk suite and the Dvirsk suite outcrop in the Akhaltsikhsk depression.

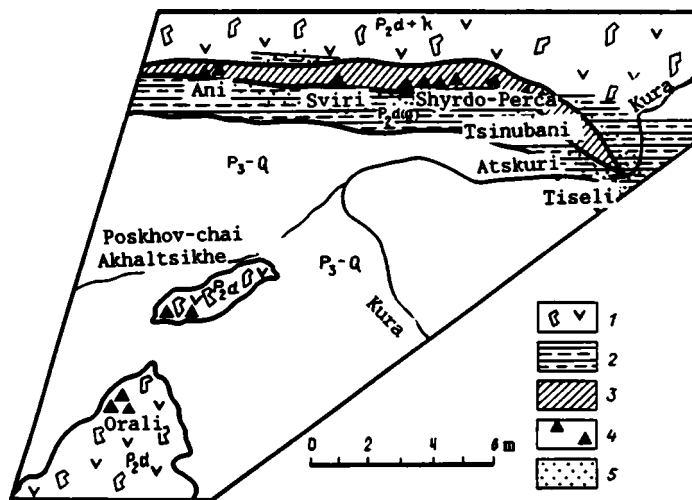


Fig. 1. A geological map of the region of agate-chalcedonic and zeolite deposits of Meskhetiya. 1) andesitic-basaltic and basaltic tuffobreccias and agglomerates; 2) layered tufts and tephroids; 3) dellenitic horizon; 4) agate-chalcedonic deposits and shows; 5) volcanogenic-exhalational zeolitization. P_2d+k) Middle Eocene, Dvirsk and Kvabiskhevsk suites; P_2d) Middle Eocene, Dvirsk suite; $P_2d(g)$) Middle Eocene, Dvirsk suite (Gurkel'sk facies); P_3-Q) Upper Eocene-Quaternary rocks.

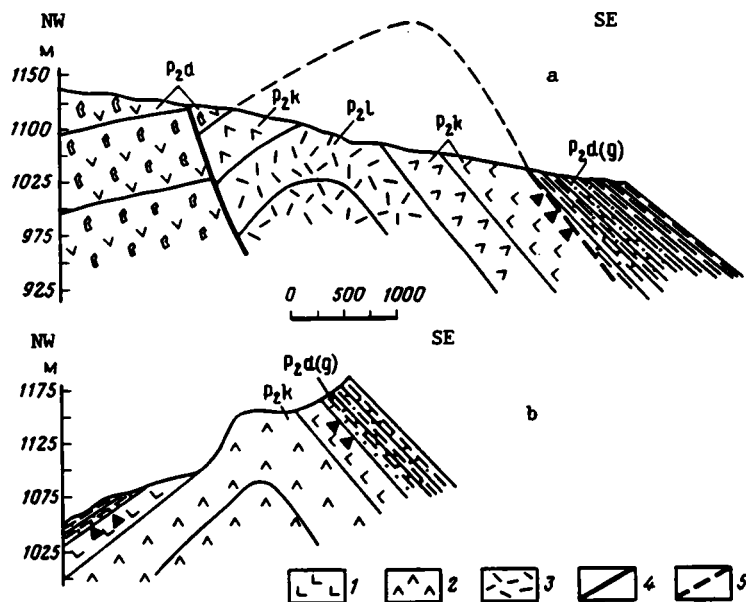


Fig. 2. Geological sections of the Ushcheliya River in Tsinubnistskali (a) and Tiseli (b). 1) dellenitic horizon; 2) lavas and hyaloclastics of the Kvabiskhevsk suite; 3) layered tufts, tuffobreccias, and lavas of the Likansk suite; 4) fault line; 5) line of discordance; P_2l) Middle Eocene, Likansk suite; P_2k) Middle Eocene, Kvabiskhevsk suite. See Fig. 1 for remaining symbols.

Stratiform zeolite deposits and agate-chalcedonic deposits lie exclusively in the upper layers of the Kvabiskhevsk suite (within the dellenitic horizon) and in the Dvirsk suite (Figs. 1 and 2). The largest of these deposits are located on the southern slope of the Adzhar-Imeretia Range and on the southeastern limb of the Borzhomi-Abastumansk anticlinal structure, with an axis extending in a sublatitudinal direction for many tens of kilometers. The agate-chalcedonic deposits and shows of the Shurdoisk group (Svir, Boga, Agara, Shurdo, Tsinubani, Tiseli, etc.)

coincide with zones of crushing and argillization in the dellenites. The stratiform zeolite beds lie within tephroids of the Gurkel'sk facies in the Dvirsk suite located above the dellenitic horizon (see Figs. 1 and 2). The dellenitic horizon itself concludes the Kvabiskhevsk suite of lava crusts and consists of pitch-black and rose-gray lavas with a pitchstone appearance and are the product of a fissure eruption. They extend in a sublatitudinal direction for 30 km from Tiseli village to the Abastumani health resort [10].

There is no unity of opinion among investigators concerning the ages of the pitch-black and rosy dellenites and the chalcedony formation. Some authors propose a significant separation in time between the chalcedony formation and the formation of the enclosing Middle Eocene stratum, genetically associating the chalcedony formation with that of the Miocene rosy andesites cross-cutting rocks. They identify the rosy andesites with the rose-gray dellenites cross-cutting the pitch-black rocks of the dellenitic horizon [1, 12, 14]. However, the Middle-Eocene Age for the chalcedony formation of the Shurdoisk group has not been questioned for a long now [6, 8]. In addition to the geological data (the mutual cross-cutting and interstratification of the rosy and pitch-black dellenites), the evidence includes the potassium-argon ages of these rocks (48.5 and 42 million years respectively) and also the absolute ages of the apophyllite and the native silica associated with the minerals in the agate-containing amygdaloids. Taking into account a correction for the coefficient proposed by F. V. Chukhrov et al., [11], the age of the apophyllite amounts to 40.3-46.5 million years.*

The limbs of the Borzhomi-Abastumansk anticlinal structure are lithologically dissimilar (Fig. 2). The southeastern limb is composed of lavas and hyaloclastics of the Kvabiskhevsk suite completing the dellenitic horizon, followed by packets of thin-layered silty-sandy and silty tuffs tuffites of a tephroid appearance (interstratified with thin layers of pelitomorphic limestones and marls) known as the Gurkel'sk facies of the Dvirsk suite. On the northwestern limb, the Kvabiskhevsk suite consists of lavas and hyaloclastics of basaltic, andesitic-basaltic, and andesitic compositions. The dellenitic horizon is absent here and, in contrast to the Gurkel'sk tephroid facies of the southern limb, the Dvirsk suite, represented by massive, rudaceous tuffobreccias and agglomerates of andesitic-basaltic compositions, lies above the Kvabiskhevsk suite. The agate-chalcedonic and zeolite deposits are located on the southeastern limb (Fig. 2, whereas, chalcedony mineralization is absent to the northwest and zeolitization (laumontite, analcime, and natrolite) occur only along crush zones in the form of thin veinlets.

The agate-chalcedonic deposits of the Pamachsk group (Orali, Ziareti, Borbalo), located in the Akhaltsikhsk depression (Fig. 1), differs from the Shurdoisk group with respect to conditions of deposition and composition of the enclosing rocks. These deposits lie within the Dvirsk suite. The country rocks associated with these deposits have an andesitic-basaltic composition and are represented by rudaceous tuffobreccias and agglomerates with thicknesses exceeding 500 m in the vicinity of Orali. They are distinguished by extremely irregular grain-sizes of fragments and consist of accumulations of 1.5-2-meter blocks cemented with finely fragmental material. The agglomerates and breccias cross-cut dikes, veins and stocks of andesitic and andesitic basaltic compositions. All this suggests the presence of deposits of an Eocene volcanic center within the region, and the country rocks themselves are a typical peri-vent facies.

Agate-chalcedonic mineralization in association with zeolites (laumontite, heulandite, and mordenite) and with calcite occur in crush zones within the loose cement of the agglomerates. In addition, opal and chalcedony form pseudomorphs after the remains of trees buried in the agglomerates [5, 7, 13]. The presence of these suggests subaerial conditions of eruption and chalcedony formation.

The productive zeolite deposits contain from 55 to 95% clinoptilolite. The thicknesses of individual, commercial beds within the different deposits vary from 3 to 15 m; the total thickness of such beds reaches 30 m. The largest of the beds, the Tisel'sk, was recently discovered by coworkers at the Geological Institute of Academy of Sciences of the USSR, T. V. Batiashvili and G. A. Mikadze; it has a total thickness of clinoptilolitized beds equaling more than 50 m and contains a high content (from 55 to 95%) of clinoptilolite. Taking into account that the deposit does not contain unproductive layers and that layers containing from 70 to 85% clinoptilolite predominate, the deposit should be considered higher perspective.

*The potassium-argon measurements were carried out at the Laboratory of Geochronology and Nuclear Studies of the Institute of Geological Sciences, Academy of Sciences of the Armenian SSR under the directorship of G. P. Bagdasaryan.

TABLE 1. Chemical Compositions of Fresh and Altered Pitch-Black Dellenites, %

Sample No.	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	MnO	MgO	CaO
1	61,80	0,40	13,40	1,96	0,90	0,10	1,33	2,51
2	61,12	0,53	14,27	3,16	1,8	0,14	—	3,01
3	58,40	0,25	15,49	2,33	0,54	0,03	1,06	4,16
4	55,18	0,09	14,79	2,21	1,08	0,06	1,80	4,21
5	57,58	0,45	14,73	1,43	0,40	0,03	1,47	4,60
6	55,58	0,28	15,32	2,33	0,54	0,03	2,89	3,78
7	53,27	0,52	14,32	3,14	0,50	0,07	3,06	3,60
8	55,86		13,94	4,89	0,72	0,04	3,91	1,93

Sample No.	N ₂ O	K ₂ O	P ₂ O ₅	SO ₃	H ₂ O	Heat loss	Σ	Specific gravity
1	4,00	4,00	0,11		2,50	6,98	99,99	2,20
2	3,52	2,80	0,01	0,20	3,3	6,3	100,16	2,27
3	0,85	1,03	0,05		7,86	7,64	99,69	1,72
4	1,28	2,09	0,07	0,15	6,46	10,30	99,77	2,03
5	1,50	2,10	0,12	—	5,80	10,12	100,33	1,82
6	0,66	0,76	0,09	—	9,15	8,41	99,82	1,74
7	1,30	1,40	0,13	—	9,52	9,12	99,95	1,80
8	0,09	1,06		0,04	3,80	13,32		

Explanation. Samples: 1, 2) unaltered dellenites; 3-5) intensively zeolitized (heulandite) and montmorillonitized dellenites; 6, 7) from unconsolidated sites within one and the same zone with a predominance of montmorillonite; 8) pelitic fraction obtained from intensively argillized zone within the dellenites. Analytical chemists: L. Basiashvili, G. Tarkhnishvili, and V. Chitaishvili.

TABLE 2. Frequencies of Major IR Absorption Bands, cm⁻¹

Sample No.	Si—O	Si—O	Si—O—Al	Al—O	Si—O—Si	Si—O	Al—OH	Si—O	Si—O
1	440	470	525	—	780	840	920	1040	—
2	440	470	525	625	780	—	—	1040	1150
3	440	470	525 (weak)	625	780	—	—	1040	1205
4	440	470	525	625	780	—	920	1040	—
5	—	470	525 (very weak)	625	780	—	—	1040	1205
6	—	470	525 (weak)	625	780		920	1040	—
7	440	470	525	625	780	840	920	1040	—

Explanation. Samples: 1) pelitic fraction obtained from intensively argillized zone in dellenites; 2, 4, 7) from unconsolidated areas of the zone with a predominance of montmorillonite; 3, 5, 6) intensively zeolitized (heulandite) and montmorillonitized dellenites. T. A. Gvakhariya, analytical chemist.

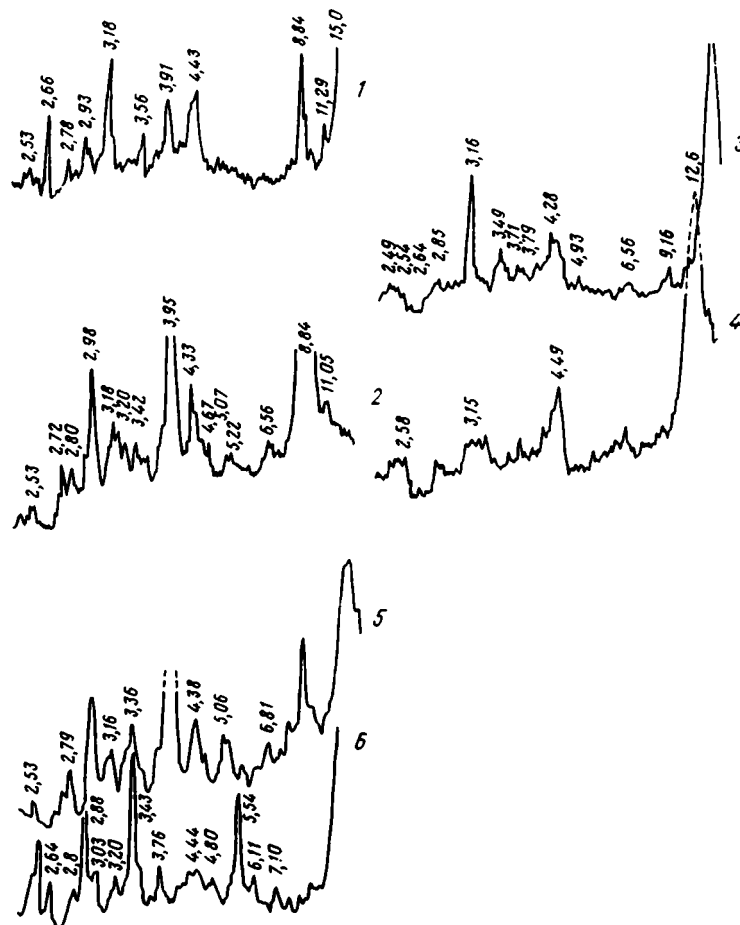


Fig. 3. X-ray diffraction patterns of pitch-black dellenites from rocks subjected to volcanogenic-exhalational zeolitization (R. A. Akhvlediani, analytical chemist). 1) intensively zeolitized (heulandite) and montmorillonitized dellenite; 2) heulanditized dellenite; 3) from less areas of the zone with a predominance of montmorillonites; 5) clinoptilolite-montmorillonite tuff containing 75-85% clinoptilolite; 6) montmorillonite-analcimized tuff.

Clinoptilolite and sometimes phillipsite beds lying upon the upper layers of the Gurkel'sk facies are widely occurring and extend for tens of kilometers along the dellenitic horizon (Fig. 1). In addition, one should note the different degrees of zeolitization with the commercial layers and also the significant variations in their thicknesses within different areas.

The Material Composition of the Agate-Chalcedonic and Zeolite Deposits

The agate-chalcedonic mineralization infills the voids within crush zones, composes amygdaloids, metasomatically replaces the tree trunks and branches buried in the agglomerates and tuffobreccias, and fills interspherulitic spaces. Minerals of active silica (opal, chalcedony, quartz, and lussatite) associate with the zeolites (erionite, heulandite, and mordenite), with calcite, apophyllite, barite, etc.

The largest deposits (The Shurdoisk group) coincide with zones of crushing and argillization within the dellenites composing the Agatonosnyi horizon.

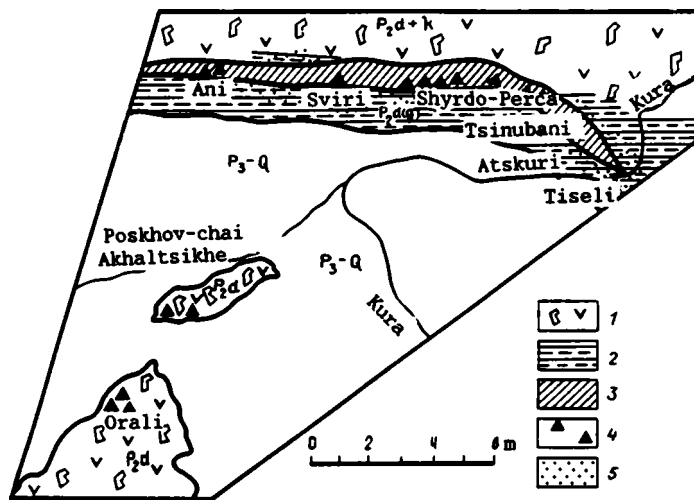


Fig. 1. A geological map of the region of agate-chalcedonic and zeolite deposits of Meskhetya. 1) andesitic-basaltic and basaltic tuffobreccias and agglomerates; 2) layered tufts and tephroids; 3) dellenitic horizon; 4) agate-chalcedonic deposits and shows; 5) volcanogenic-exhalational zeolitization. P_2d+k) Middle Eocene, Dvirsk and Kvabiskhevsk suites; P_2d) Middle Eocene, Dvirsk suite; $P_2d(g)$) Middle Eocene, Dvirsk suite (Gurkel'sk facies); P_3-Q) Upper Eocene-Quaternary rocks.

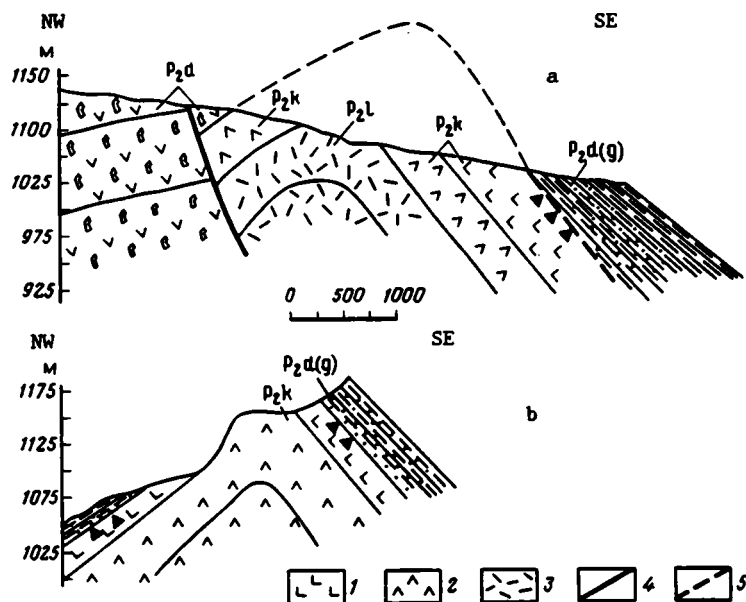


Fig. 2. Geological sections of the Ushcheliya River in Tsinubnistskali (a) and Tiseli (b). 1) dellenitic horizon; 2) lavas and hyaloclastics of the Kvabiskhevsk suite; 3) layered tufts, tuffobreccias, and lavas of the Likansk suite; 4) fault line; 5) line of discordance; P_2l) Middle Eocene, Likansk suite; P_2k) Middle Eocene, Kvabiskhevsk suite. See Fig. 1 for remaining symbols.

Stratiform zeolite deposits and agate-chalcedonic deposits lie exclusively in the upper layers of the Kvabiskhevsk suite (within the dellenitic horizon) and in the Dvirsk suite (Figs. 1 and 2). The largest of these deposits are located on the southern slope of the Adzhar-Imeretia Range and on the southeastern limb of the Borzhomi-Abastumansk anticlinal structure, with an axis extending in a sublatitudinal direction for many tens of kilometers. The agate-chalcedonic deposits and shows of the Shurdoisk group (Svir, Boga, Agara, Shurdo, Tsinubani, Tiseli, etc.)

coincide with zones of crushing and argillization in the dellenites. The stratiform zeolite beds lie within tephroids of the Gurkel'sk facies in the Dvirsk suite located above the dellenitic horizon (see Figs. 1 and 2). The dellenitic horizon itself concludes the Kvabiskhevsk suite of lava crusts and consists of pitch-black and rose-gray lavas with a pitchstone appearance and are the product of a fissure eruption. They extend in a sublatitudinal direction for 30 km from Tiseli village to the Abastumani health resort [10].

There is no unity of opinion among investigators concerning the ages of the pitch-black and rosy dellenites and the chalcedony formation. Some authors propose a significant separation in time between the chalcedony formation and the formation of the enclosing Middle Eocene stratum, genetically associating the chalcedony formation with that of the Miocene rosy andesites cross-cutting rocks. They identify the rosy andesites with the rose-gray dellenites cross-cutting the pitch-black rocks of the dellenitic horizon [1, 12, 14]. However, the Middle-Eocene Age for the chalcedony formation of the Shurdoisk group has not been questioned for a long now [6, 8]. In addition to the geological data (the mutual cross-cutting and interstratification of the rosy and pitch-black dellenites), the evidence includes the potassium-argon ages of these rocks (48.5 and 42 million years respectively) and also the absolute ages of the apophyllite and the native silica associated with the minerals in the agate-containing amygdaloids. Taking into account a correction for the coefficient proposed by F. V. Chukhrov et al., [11], the age of the apophyllite amounts to 40.3-46.5 million years.*

The limbs of the Borzhomi-Abastumansk anticlinal structure are lithologically dissimilar (Fig. 2). The southeastern limb is composed of lavas and hyaloclastics of the Kvabiskhevsk suite completing the dellenitic horizon, followed by packets of thin-layered silty-sandy and silty tuffs tuffites of a tephroid appearance (interstratified with thin layers of pelitomorphous limestones and marls) known as the Gurkel'sk facies of the Dvirsk suite. On the northwestern limb, the Kvabiskhevsk suite consists of lavas and hyaloclastics of basaltic, andesitic-basaltic, and andesitic compositions. The dellenitic horizon is absent here and, in contrast to the Gurkel'sk tephroid facies of the southern limb, the Dvirsk suite, represented by massive, rudaceous tuffobreccias and agglomerates of andesitic-basaltic compositions, lies above the Kvabiskhevsk suite. The agate-chalcedonic and zeolite deposits are located on the southeastern limb (Fig. 2, whereas, chalcedony mineralization is absent to the northwest and zeolitization (laumontite, analcime, and natrolite) occur only along crush zones in the form of thin veinlets.

The agate-chalcedonic deposits of the Pamachsk group (Orali, Ziareti, Borbalo), located in the Akhaltsikhsk depression (Fig. 1), differs from the Shurdoisk group with respect to conditions of deposition and composition of the enclosing rocks. These deposits lie within the Dvirsk suite. The country rocks associated with these deposits have an andesitic-basaltic composition and are represented by rudaceous tuffobreccias and agglomerates with thicknesses exceeding 500 m in the vicinity of Orali. They are distinguished by extremely irregular grain-sizes of fragments and consist of accumulations of 1.5-2-meter blocks cemented with finely fragmental material. The agglomerates and breccias cross-cut dikes, veins and stocks of andesitic and andesitic basaltic compositions. All this suggests the presence of deposits of an Eocene volcanic center within the region, and the country rocks themselves are a typical peri-vent facies.

Agate-chalcedonic mineralization in association with zeolites (laumontite, heulandite, and mordenite) and with calcite occur in crush zones within the loose cement of the agglomerates. In addition, opal and chalcedony form pseudomorphs after the remains of trees buried in the agglomerates [5, 7, 13]. The presence of these suggests subaerial conditions of eruption and chalcedony formation.

The productive zeolite deposits contain from 55 to 95% clinoptilolite. The thicknesses of individual, commercial beds within the different deposits vary from 3 to 15 m; the total thickness of such beds reaches 30 m. The largest of the beds, the Tisel'sk, was recently discovered by coworkers at the Geological Institute of Academy of Sciences of the USSR, T. V. Batiashvili and G. A. Mikadze; it has a total thickness of clinoptilolitized beds equaling more than 50 m and contains a high content (from 55 to 95%) of clinoptilolite. Taking into account that the deposit does not contain unproductive layers and that layers containing from 70 to 85% clinoptilolite predominate, the deposit should be considered higher perspective.

*The potassium-argon measurements were carried out at the Laboratory of Geochronology and Nuclear Studies of the Institute of Geological Sciences, Academy of Sciences of the Armenian SSR under the directorship of G. P. Bagdasaryan.

TABLE 1. Chemical Compositions of Fresh and Altered Pitch-Black Dellenites, %

Sample No.	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	MnO	MgO	CaO
1	61,80	0,40	13,40	1,96	0,90	0,10	1,33	2,51
2	61,12	0,53	14,27	3,16	1,8	0,14	—	3,01
3	58,40	0,25	15,49	2,33	0,54	0,03	1,06	4,16
4	55,18	0,09	14,79	2,21	1,08	0,06	1,80	4,21
5	57,58	0,45	14,73	1,43	0,40	0,03	1,47	4,60
6	55,58	0,28	15,32	2,33	0,54	0,03	2,89	3,78
7	53,27	0,52	14,32	3,14	0,50	0,07	3,06	3,60
8	55,86		13,94	4,89	0,72	0,04	3,91	1,93

Sample No.	N ₂ O	K ₂ O	P ₂ O ₅	SO ₃	H ₂ O	Heat loss	Σ	Specific gravity
1	4,00	4,00	0,11		2,50	6,98	99,99	2,20
2	3,52	2,80	0,01	0,20	3,3	6,3	100,16	2,27
3	0,85	1,03	0,05	—	7,86	7,64	99,69	1,72
4	1,28	2,09	0,07	0,15	6,46	10,30	99,77	2,03
5	1,50	2,10	0,12	—	5,80	10,12	100,33	1,82
6	0,66	0,76	0,09	—	9,15	8,41	99,82	1,74
7	1,30	1,40	0,13	—	9,52	9,12	99,95	1,80
8	0,09	1,06		0,04	3,80	13,32		

Explanation. Samples: 1, 2) unaltered dellenites; 3-5) intensively zeolitized (heulandite) and montmorillonitized dellenites; 6, 7) from unconsolidated sites within one and the same zone with a predominance of montmorillonite; 8) pelitic fraction obtained from intensively argillized zone within the dellenites. Analytical chemists: L. Basiashvili, G. Tarkhnishvili, and V. Chitaishvili.

TABLE 2. Frequencies of Major IR Absorption Bands, cm⁻¹

Sample No.	Si—O	Si—O	Si—O—Al	Al—O	Si—O—Si	Si—O	Al—OH	Si—O	Si—O
1	440	470	525	—	780	840	920	1040	—
2	440	470	525	625	780	—	—	1040	1150
3	440	470	525 (weak)	625	780	—	—	1040	1205
4	440	470	525	625	780	—	920	1040	—
5	—	470	525 (very weak)	625	780	—	—	1040	1205
6	—	470	525 (weak)	625	780		920	1040	—
7	440	470	525	625	780	840	920	1040	—

Explanation. Samples: 1) pelitic fraction obtained from intensively argillized zone in dellenites; 2, 4, 7) from unconsolidated areas of the zone with a predominance of montmorillonite; 3, 5, 6) intensively zeolitized (heulandite) and montmorillonitized dellenites. T. A. Gvakhariya, analytical chemist.

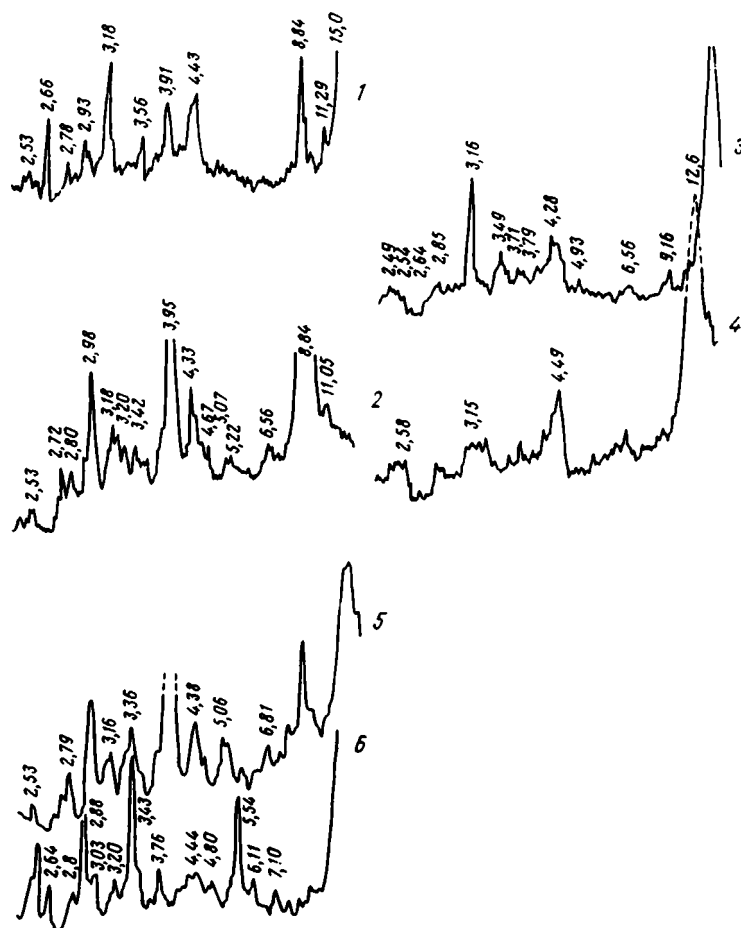


Fig. 3. X-ray diffraction patterns of pitch-black dellenites from rocks subjected to volcanogenic-exhalational zeolitization (R. A. Akhvlediani, analytical chemist). 1) intensively zeolitized (heulandite) and montmorillonitized dellenite; 2) heulanditized dellenite; 3) from less areas of the zone with a predominance of montmorillonites; 5) clinoptilolite-montmorillonite tuff containing 75-85% clinoptilolite; 6) montmorillonite-analcimized tuff.

Clinoptilolite and sometimes phillipsite beds lying upon the upper layers of the Gurkel'sk facies are widely occurring and extend for tens of kilometers along the dellenitic horizon (Fig. 1). In addition, one should note the different degrees of zeolitization with the commercial layers and also the significant variations in their thicknesses within different areas.

The Material Composition of the Agate-Chalcedonic and Zeolite Deposits

The agate-chalcedonic mineralization infills the voids within crush zones, composes amygdaloids, metasomatically replaces the tree trunks and branches buried in the agglomerates and tuffobreccias, and fills interspherulitic spaces. Minerals of active silica (opal, chalcedony, quartz, and lussatite) associate with the zeolites (erionite, heulandite, and mordenite), with calcite, apophyllite, barite, etc.

The largest deposits (The Shurdoisk group) coincide with zones of crushing and argillization within the dellenites composing the Agatonosnyi horizon.

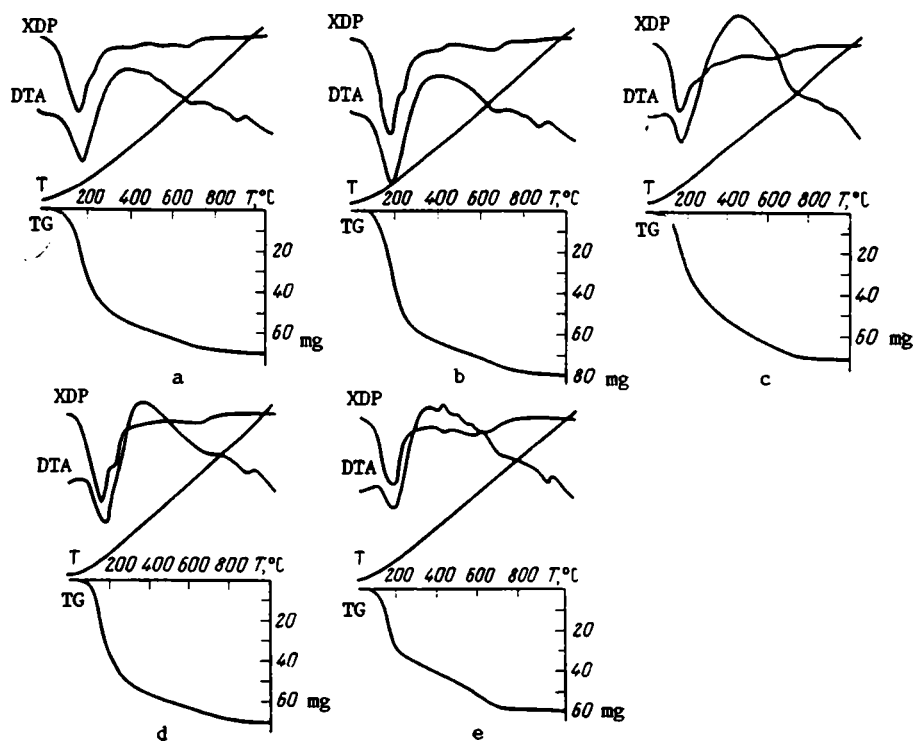


Fig. 4. Derivatograms of altered pitch-black dellenites (T. V. Batiashvili, analytical chemist). a) comparatively weakly layered dellenite; b-d) from unconsolidated areas of intensive zeolitized and montmorillonitized dellenites; e) pelitic fraction obtained from intensively argillized zones within the dellenites.

The dellenites form a covering, lenticular deposit of complex structure consisting of a multitude of caked, thin, repeated, pulsating fissure eruptions of lava [10, 12]. They are glassy rocks of mandelstone texture. The pitch-black color of the dellenites is due to the abundance of glass (more than 85% of the total volume of the rock) and the fine grains and other fines of magnetite disseminated within it. The volcanic glass has an acidic composition (SiO_2 on the order of 70%, $N \sim 1.504-1.507$) and possesses a well expressed perlitic microtexture. Porphyritic inclusions are represented by oligoclase (7-10%), augite (3-5%), and, more rarely, hypersthene. The high content of K_2O (2.8-4%) and SiO_2 (61%) in the absence of potassium-bearing minerals (the K_2O is completely contained within the mass of the rock), allows these rocks to be classified as subalkaline rocks, dellenites, as understood by A. N. Zavaritskov.

Another variety of rocks are involved in the make-up of the Agatonosnii horizon. These are rose-gray dellenites the rusts of which are interstratified with the pitch-black dellenites. They also form cross-cutting subvolcanic bodies (veins, dikes, necks, and stocks). The rose-gray glauconites are well crystallized, very dense rocks. As in the case of the pitch-black lavas, they subsequently came to possess a well expressed porphyritic texture. But, in contrast to the pitch-black dellenites, the groundmass in the rose-gray rocks is crystallized to a greater degree and consists of a multitude of acid-plagioclase and pyroxene microliths buried within the glassy mass and tinted rose-brown with iron hydrates.

As a result of hydrothermal processes (zeolitization, montmorillonitization, silicification), the pitch-black dellenites are strongly disintegrated, thinned-out, and layered along the crush zones. Locally, there is intensive silicification of the argillized zones, and the rocks take on a jasper-like appearance. The perlitic microtexture of the dellenites is often preserved in the zones of alteration. In these very zones, argillization alters the rock almost totally. Within the dellenites, one can observe the entire gamut from almost completely argillized and zeolitized dellenites to practically unaltered dellenites with fresh volcanic glass. The petrochemical composition of the rock varies correspondingly (Table 1).

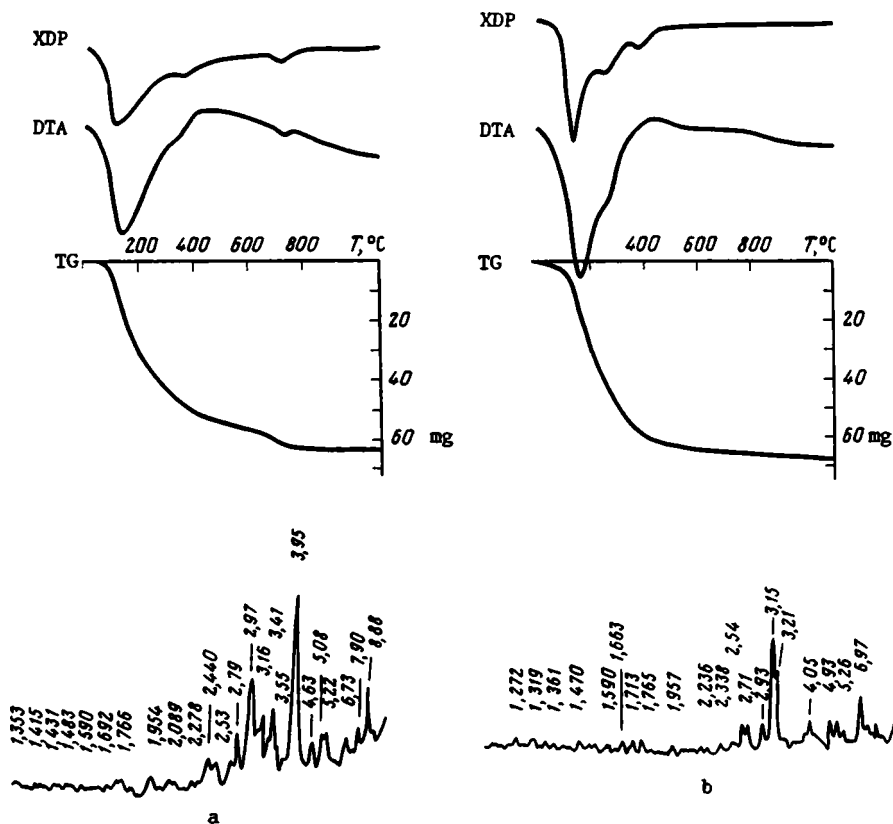


Fig. 5. Derivative patterns and diffraction pattern of clinoptilolite (a) and phillipsite (b) from deposits of the narrow of the Tsinubnistskali River (according to the data of T. V. Batiashvili and G. A. Mikadze).

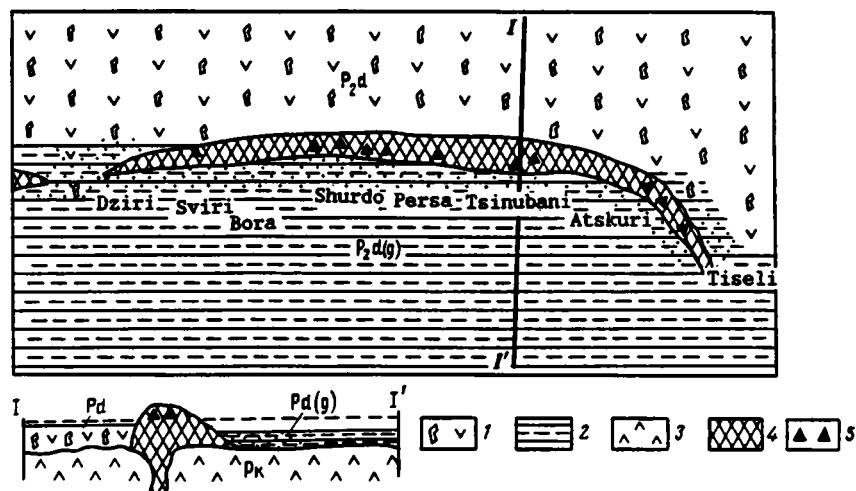


Fig. 6. Paleogeographic representation of the "Dvirsk Sea." 1, 2) Basins of volcanic and tephroid sedimentation respectively; 3) sea bottom (Kvabiskhevsk suite); 4) dellenitic ridge; 5) sea surface. For other designations, see Fig. 1.

During the montmorillonitization of the dellenites, intensive removal of silica and alkali from the rock takes place [6, 8, 14]. It was previously suggested [14] that this was the single source of silicic acid for chalcedony formation. However, it was later shown that silicic acid is removed abundantly from the underlying deposits of volcanic formations during the process of their low-temperature propylitization and zeolitization [6, 8]; evidence of

this includes the chalcedony shows in the Pamachsk group and the Rustavi deposits, where agate-chalcedonic mineralization is in no way connected with argillized zones and gravitates toward cavities in andesitic-basaltic agglomerates and toward interspherulitic spaces in plagiobasaltic lavas [6, 8].

The mineral composition of the ore-enclosing argillized and zeolitized zones of dellenites were investigated using methods of x-ray structural and thermographic analysis along with Infrared spectroscopy.

Two zeolite phases primarily occur on the x-ray diffraction patterns from the ore-enclosing zones of crushing and hydrothermal alteration: the phase of the heulandite group ($d = 8.84, 3.91\text{--}3.95, 2.93\text{--}2.98 \text{ \AA}$) and the montmorillonite group ($d = 15.00, 14.7, 12.6, 4.44\text{--}4.49 \text{ \AA}$). With an increase in the intensity of the hydrothermal alternation and disintegration, the clay phase begins to predominate (Fig. 3, x-ray diffraction pattern 3 with a well-expressed peak at $14.73 \text{ \AA}$). The pelitic fraction from the intensively argillized area of the ore-enclosing zone primarily consists of montmorillonite (Fig. 3, diffraction pattern 4).

The differential heating curves of the rock samples from the zones of intensive zeolitization and montmorillonitization (Fig. 4a-d) are generally similar. An intensive endothermal effect with a maximum at $170\text{--}180^\circ\text{C}$ occurs on the DTA curve within the interval from 100 to 400°C , this corresponds to a removal of absorbed water and the significant weight loss visibly expressed on the XDP and TG curves. The next weak endothermal effect occurs in the intermediate-temperature region ($500\text{--}700^\circ\text{C}$). It has a maximum at approximately 700°C and is connected with the removal of the water's hydroxyl group and reflects an additional loss of weight. The total loss of weight amounts to $17\text{--}19.5\%$.

A high level of hydration and appreciable (17.72%) loss of weight is characteristic of the pelitic fraction obtained from strongly argillized dellenites (Fig. 4d) and identified by x-ray diffraction as montmorillonite (Fig. 3, diffraction pattern 4). In addition to the three endoeffects mentioned, there is an exothermal effect at $400\text{--}420^\circ\text{C}$ on the DTA curve of this sample (immediately after the second endoeffect); this could be connected with the oxidation of pyrite. The next weak exoeffect occurs immediately after the third endothermal effect at a temperature of $920\text{--}940^\circ\text{C}$ and is apparently connected with the crystallization of the amorphous decomposition products of the montmorillonite.

A comparison of the XDP and TG curves with the DTA curve in the samples investigated suggests that the endothermal effects are due to the liberation of water. The XDP and TG curves indicate that water liberation took place in stages with significant liberation of water during the first intensive endoeffect. The differential heating curves confirm the predominantly montmorillonitic character of the unconsolidated products from the zones of intensive alteration of dellenites; this is in accordance with the data from the x-ray diffraction analysis (Fig. 3).

The IR absorption spectra of the samples studied are similar in many respects. In all of these spectra, one can trace absorption bands within the $440, 470, 525, 625, 780, \text{ and } 1040 \text{ cm}^{-1}$ regions corresponding to valent and deformational oscillations of Si-O , Si-O-Si , Si-O-Al and other bonds (Table 2). Some differences in IR spectra are due to differences in the composition of the samples studied. thus, strong absorption glands in the regions 470 and 525 cm^{-1} and an absorption band at 920 in the form of a shoulder are characteristic of montmorillonite. When there is predominance of zeolites, the absorption in the region of 1040 cm^{-1} broadens and shoulders appears at 1150 cm^{-1} and 1205 cm^{-1} . The data obtained are confirmed by the phase compositions of the samples investigated (Fig. 3).

The rose-gray dellenites were also subjected to hydrothermal alteration, although to a significantly lesser degree than the pitch-black dellenites. Within crush zones (the Arara area), the cement of the "breccia" is primarily represented by silica and calcite (a dense network of diversely oriented silica-calcite veinlets gives the rock the appearance of a breccia).

The relative resistance of the rose-gray dellenites to the influence of the hydrothermal solutions can be explained by the lesser brecciation and greater crystallization of these rocks when compared to the pitch-black dellenites.

The zones of argillization and zeolitization within the dellenitic horizon contain agate separations of various morphological types: amygdaloids which are solidly or partially filled (geodes), cluster-like separations, veinlets, etc. The agate separations are extremely irregular and are scattered through the total mass of the enclosing rock without any pattern. They are infilled with diverse low-temperature minerals, often forming series of sequential growths. The minerals include silica (opal, chalcedony, quartz, amethyst, etc.), zeolites (erionite, heulandite, mordenite), calcite (and sometimes aragonite), and, more rarely, apophyllite, barite, and sometimes sulfides.

The secretions are distinguished by a special diversity of internal morphology. Their external forms are controlled by the shape of the enclosing cavity, and the mineral composition is wholly dependent upon the regime associated with the solution's entry into the cavity and the solutions' physicochemical parameters. Secretions with

solid, homogeneous infilling, geodes, and secretions with concentric and place-parallel arrangements of layers are formed as a consequence of this. Transitional varieties also occur.

There are both mono- and polymineralic formations, but the latter generally predominate. While studying mineral aggregates from the cavities in the agate-enclosing rocks, a number of mineral associations were discovered: opal-zeolite, zeolite-opal-chalcedony, opal-chalcedony, opal-chalcedony-quartz, opal-chalcedony-calcite, zeolite-calcite-chalcedony, zeolite-opal-chalcedony-quartz-apophyllite, etc. In the agate formations themselves, one can see repeated manifestations of tectonic movements: multistage agate formations, brecciated agates, agates with difference systems of plane-parallel layers.

The stratiform zeolite deposits extend along (and parallel to) the dellenic horizon and agate-chalcedonic shows (see Figs. 1, 2) after the dellenic horizon comes a packet of layered tuffs and tuffites of a tephroid appearance interstratified with layers of marls and pelitomorphic limestones. Depending upon the degree of erosion, the thickness of this packet varies from 100 to 300 m. The tuffs and tuffites are significantly altered; however, it is primarily the cement and vitreous groundmass which is altered in the litho- and crystalloclastic varieties, whereas, the phenocrysts remain fresh. With respect to the abundance of femic minerals (pyroxene, hornblende), and with respect to the composition of the plagioclase, they are analogous to the rocks of the Dvirsk suite. The material composing them is represented by facies at a distance from the volcanic centers. Within the sections of this packet, a packet which extends for tens of kilometers along the dellenic horizon (the narrows of the Tseli, Tsinubnistskali, and Shurdos-gele rivers and the vicinity of Boga, Sviri, and Dziri villages), the lower horizons of the Gurkel'sk facies are composed of tuffs and tuffites of psammitic dimensions and lithocrystalloclastic compositions. Intensive analcimization, montmorillonitization, and carbonatization occurs along these horizons. Clinoptilolite is found here in clearly subordinate quantities (see Fig. 3, diffraction pattern 6). There is a packet of thinner-layered and finer-grained vitroclastic aleuritic and aleuropelitic tuffs located at stratigraphically higher position. Productive beds of highly-siliceous zeolites and clinoptilolite ($d = 8.84, 3.95, 3.36, \text{ and } 2.97 \text{ \AA}$) and phillipsite ($d = 6.97, 3.15, \text{ and } 2.71 \text{ \AA}$) with subordinate concentrations of montmorillonite ($d = 14.73 \text{ \AA}$) form along these tuffs (see Fig. 3, diffraction pattern 5; Fig. 5, diffraction pattern b). The total thickness of the productive beds varies from 30 to 50 m in different areas.

T. V. Batiashvili, G. A. Midadze, and V. G. Gogishvili [2] found layers of phillipsitized tuffs totally 15-20 m in thickness together with clinoptilolitized beds in areas of Tsinubnistskali, Shurdos-gele, and Tsriokhis-Tskali.

The content of clinoptilolite in different layers varies over a broad range, from 55 to 95%. The most consistent clinoptilolite content (75-85%) occurs in the Tseli area. In addition, the productive beds here are the most extensive, according to the data of T. V. Batiashvili et al., their visible extent along strike amounts to more than a mile.

Paleogeographic Environment and Genesis of the Agate-Chalcedonic and Zeolite Mineralization.

Thus, the ore-enclosing rocks of the agate-chalcedonic deposits of the Shurdoisk group are a dellenic horizon, with volcanogenic-exhalational zeolitization having occurred during the cementation of the Gurkel'sk facies of the Dvirsk suite. Let us now turn our attention to the character of sediment accumulation on the northwestern and southeastern limbs of the Borzhomi-Abastumansk anticline (Figs. 2 and 6). Within the dellenic horizon on the southern limb, one can trace the tephroid Gurkel'sk facies of the Dvirsk suite composed of sediments distant from volcanic centers. On the northern limb, the dellenic horizon is absent (Fig. 2), and the Dvirsk suite consists of massive tuffobreccias and agglomerates (the peri-vent facies).

Consequently, there is completely different character of sedimentation here. It is important to emphasize that there are rubbles of pitch-black dellenicites both within the Gurkel'sk tephroid facies (the southern limb) and in the tuffobreccias of the northern limb. The dellenic barrier's subsequent and also sharp separation of the two sedimentary basins in the Eocene sea (essentially volcanic in the north and tephroidal in the south) during "Dvirskian" time (Fig. 6) suggests the existence of a dellenic land mass which extended for tens of kilometers in a sublatitudinal direction in the form of a narrow strip.

The dellenicites are a product of a fissure eruption. At their greatest extent, corresponding to the length of a subaqueous fault, their distribution in cross-section is very modest, not exceeding 2 km (the dellenicites pinch out rapidly in a northern direction). The dellenic horizon dividing the "Dvirsk" sea did not bulge above sea level, since there are areas of occurrence of tephroid or essential volcanic facies to the north and south of the dellenic belt (Fig. 6). It is noteworthy that agate-chalcedonic mineralization is absent within the dellenicites of these regions. The formation of a dellenic barrier in the "Dvirsk" sea was unconnected with any phase of folding (for this time period,

folding is not found here); it was a result of eruptions of viscous dellenitic lava with flows and veins consisting of 85-90% volcanic glass. The barrier, therefore, did not spread, but rather created a pile along the fissure of the eruption, forming a volcanic ridge emerging at the sea's surface and dividing the "Dvirsk" sea into two basins with different types of sedimentation.

The dellenitic barrier prevented the entry of material from the northern basin of volcanic sedimentation. Therefore, the tephra and fine volcanoclastics composing the Gurkel'sk facies entered from the south, from volcanic centers situated within the Akhaltsikhsk depression, where the Dvirsk suite was composed of essentially volcanic formations (see Fig. 1): massive tuffobreccias, agglomerates, and lavas. One of these centers was rebuilt within the region of the Pamachsk group of agate-chalcedonic deposits (Orali, Ziareti, and Borbalo). In addition, there were surface volcanic eruptions under conditions associated with a volcanic island here. The island emerged as a result of an abundant accumulation of agglomerates and tuffobreccias around a central-type volcano. Opalized and chalcedonized remnants of trees buried in the agglomerates and tuffobreccias suggest a subaerial environment for the eruption and the hydrothermal activity.

Within the Eocene sea of "Dvirskian" times, there was thus a dellenitic barrier emerging from the sea's surface. This barrier was a volcanic ridge dividing the sea into essentially volcanic and tephroidal basins of sedimentation. Volcanic islands rebuilt south of the boundaries of the Akhaltsikhsk depression. These islands were formed as a result of pile-ups of agglomerates and tuffobreccias around central-type volcanoes (the agate-chalcedonic deposits can be located precisely within them).

Thus, the agate-chalcedonic deposits of the Shurdoisk group occurring within dellenites, on the one hand, and the deposits of the Pamachsk group located within the andesitic-basaltic agglomerates of the Dvirsk suite, on the other, formed on dry land under subaerial conditions, whereas volcanogenic-exhalational zeolitization of the sediments, accompanied by the formation of stratiform deposits of highly siliceous zeolites (clinoptilolite, phillipsite, and mordenite) took place under water. It is known that both chalcedony formation and high-silica zeolitization are due to interspersions of silicic-acid solutions [9]. Zeolitization takes place in an alkaline environment (pH 8-10). Alkaline solutions favor the solubility and mobility of silica; acidification of the solutions facilitates the precipitation of silicic acid in the form of silica minerals (quartz, opal, lussatite, chalcedony, etc.). The most favorable conditions for acidification of the solutions arises under surface conditions. This is connected with the oxidation of the hydrogen sulfide in the solutions and volcanic emanations to sulfuric acid. Native silica is precipitated in cavities from acidic solutions interspersed with silicic acid. Agate-chalcedonic accumulations are formed in the process. There is a zonality associated with the mineral formation within the cavities suggestive of the following sequence: opal (lussatite) and zeolites (heulandite, erionite) are initially precipitated, zones consisting exclusively of silica minerals (chalcedony, including chalcedony with agate patterns, quartz, rock crystal, and amethyst) then followed. Calcite and apophyllite precipitated during the latter stages, often together with zeolites [7, 8]. This sequence was sometimes periodically repeated, although with the precipitation of several zones. This indicates a pulsational supply of mineral-forming solutions and change in their parameters. However, the abundance and sharp predominance of minerals of native silica is connected with the circulation of predominantly acidic solutions.

The volcanogenic-exhalational zeolitization of the reworked tephra and fine volcanoclastics took place under the influence of seawater activated by volcanic emanations upon the sediment. At the start of the sedimentation (when accumulation of psammitic material of crystallolithoclastic tuffs predominated), analcimization and montmorillonitization of the sediment took place. The productive beds contain up to 15-20% montmorillonite. Since the formation of the montmorillonite, in contrast to the formation of the zeolites, occurs in a neutral environment, accompanied by significant removal of silica and alkaline metals from the rocks (Table 1), the parameters of the solution were not consistently stable during the formation of the productive beds; they varied at times; neutralization of the solution and a decrease in the solution's silicic-acid content took place. It is known that a region of zeolite replaces a region of minerals with layered structure (clays and micas) when the pH of the solutions are lowered [9]. In analogy, an overall tendency toward increased silicic-acid content and alkalinity with increasing concentration of cations could be presumed during the volcanogenic-exhalational alteration of the sediment during the time of its deposition and diagenesis from predominately montmorillonitized layers (lower levels of the section within the tephroids of the Gurkel'sk facies of the Dvirsk suite) to the clinoptilolitized beds at its upper levels.

The rudaceous, massive Dvirsk suite on the northwestern limb of the Borzhomi-Abastumansk anticline was layered in a completely different fashion. Stratiform productive beds of highly siliceous zeolites are absent here, as well as agate-chalcedonic mineralization. Sedimentation took place under water and zeolitization (laumontite,

analcime, and desmine) and carbonatization (calcite) are primarily epigenetic and occur along crush zones and the cement of the breccias.

Consequently, the agate-chalcedonic deposits formed under conditions of surface volcanic activity. The areas of dry land (islands) within the Eocene sea should be reconstructed for organized exploration of these deposits. On the other hand, favorable conditions for deposits of highly siliceous zeolites were created on portions of the sea bottom with sporadic sedimentation of reworked tephra and fine vitroclastics. Such a situation was created in the "Dvirsk" sea where a dellenitic barrier prevented the entry of coarse volcanic material from the north and where the proximity of volcanic foci supplying exhalational solutions facilitated intensive zeolitization of the sediments.

LITERATURE CITED

1. N. A. Arkad'ev, "Conditions associated with the formation of certain agate deposits in the trans-Caucasus," *Zap. Leningr. Gos. Univ.*, **49**, 2, 165-170 (1965).
2. T. V. Batiashvili, G. A. Mikadze, and V. G. Gogishvili, "Stratiform zeolite deposits of Meskheti," *Izv. Akad. Nauk SSSR, Ser. Geol.*, No. 4, 112-120 (1985).
3. P. B. Vainerman and A. S. Smirnova, "Patterns of distribution of workable agate within the trans-Caucasus territory," *Tr. VNIISIMS*, **8**, 135-148 (1964).
4. G. V. Gvakhariya, *The Zeolites of Georgia* [in Russian], Akad. Nauk SSSR, Tbilisi (1951).
5. S. S. Gorbunov, "Concerning a certain morphological peculiarity of agates," *Handbook of the Institute of Rock Mechanics, Academy of Sciences of the USSR* (1951), pp. 27-39.
6. V. I. Gugushvili, "Post-volcanic process and formation of mineral deposits in ancient island arcs and intra-arc rifts (based on the example of the Adzhar-Trialetsk zone of the Caucasus)," *Tr. Geol. Inst., Nauk Akad. Nauk SSSR Nov. Ser.*, 1980, No. 68.
7. Ts. Sh. Kargareli, "Some questions concerning the mineralogy of the agate deposits of Meskheti," *Tr. Geol. Inst., Nauk Akad. Nauk SSSR Nov. Ser.*, 1974, No. 43, pp. 50-61.
8. Ts. Sh. Kargareli, M. G. Tatishvili, and V. I. Gugushvili, "Agate-chalcedonic mineralization within the Eocene rocks of Meskheti," *Tr. Geol. Inst., Nauk Akad. Nauk SSSR Nov. Ser.*, 1978, No. 59, pp. 7-13.
9. É. É. Senderov and N. I. Khitarov, *Zeolites, Their Synthesis and Conditions of Formation in Nature* [in Russian], Nauka, Moscow (1970).
10. M. G. Tatishvili, "Eocene volcanism of Meskheti," *Problems of the Geology of Adzhar-Trialeti* [in Russian], Metsnierba, Tbilisi (1974), pp. 39-47.
11. F. V. Chukhrov, L. P. Ermilova, and L. L. Shanin, "The problem of the age of the apophyllite in post-hydrothermal mineral associations," *Izv. Akad. Nauk SSSR, Ser. Geol.*, No. 2, 3-14 (1973).
12. B. N. Sharonov, "Peculiarities associated with the structure of the agate-bearing andesitic cover in the Akhaltsikhsk region of Georgia," *Tr. VNIIP*, **3**, 2, 47-50 (1960).
13. B. N. Sharonov, "Pipe agate and the conditions associated with its formation," *Zap. MVO*, **92**, 3, 281-291 (1963).
14. B. N. Sharonov, "The role of country rock in the formation of certain deposits of workable agate," *Zap. Leningr. Gos. Univ.*, **49**, 2, 171-179 (1965).

Based on consideration of physical processes responsible for the formation of gas hydrates, we estimate their possible implementation at depth and include observation data. Cryogenetic, transgressional, diagenetic, string-migrational, fault, elisional, hydrothermal, sedimentational, and water-mud volcanic geologic models of gas hydrate genesis are distinguished and characterized. It is shown that the most important models in which gas is concentrated are implemented in submarine conditions. It is possible to form depleted hydrate accumulations in regions with a thick cryolithozone on land and on polar shelves.

Hydrates of hydrocarbon gases at depths are interesting both as potential resources and as an unstable component of the technosphere, since their distribution may have undesirable consequences [25, 38]. It has become evident that hydrates (particularly submarine hydrates) represent a global physical-geological phenomenon which is connected with definite specifics of sedimentogenesis, lithogenesis, and the formation of underground water and heat fields [9, 24, 37]. Meanwhile, gas hydrate formation has been as yet poorly studied in geology. In particular it is unclear how natural accumulations are represented, how they can be formed, and what kind of distribution they may have.

The aim of this article is to clarify the geological processes responsible for gas hydrate formation and to determine the most effective of them.

Thus, we will consider the physical processes which may lead to hydrate formation, with the position of their implementation at depth.

There are four conditions for gas hydrate synthesis: sufficient concentration of the source materials: gas and water, sufficiently low temperature and sufficiently high pressure. Onset of any one of them in the presence of the rest serves as a cause of hydrate formation processes.

Two forms of hydrate forming systems are distinguished: the stationary, in which there is no transfer externally of the reagents which are responsible for hydrate synthesis, while the inner system is altered; and the dynamic, in which the transfer of material into the reaction zone serves as the immediate cause of the process. Generally speaking, reagents in hydrate forming system may be found in different aggregate states. However we are limited to three cases characteristic for the earth's crust: free gas + water, gas distributed in water, and free gas + ice.

We consider first the *stationary systems*. Gas hydrates may form in them as a result of cooling, compression, or increase in reagent concentration.

Cooling. The problem of gas hydrate bearing potential at depth was initially stated from the realization of the possibility of hydrate formation by exogenic lowering of the geotemperature in permafrost regions. We will call the geologic models for the formation of such hydrates *cryogenetic*, and the hydrates themselves *cryogenic*. They may arise in gas deposits (system of free gas + water), in water bearing layers (from gas saturated waters), and in sequences of permafrost rocks (in contact with ice).

We will first discuss hydrate formation in gas layers. In [7, 8, 17, 19] it is shown that complete replacement of a deposit's gas by hydrate is improbable: this is hindered by a deficit of free water and its increasing salinity, as well as by decrease in the reservoir's effective porosity and permeability by the forming hydrates. In such cases, free gas, hydrate, and water will coexist in the deposits. The transformation is accomplished more completely in massive deposits than in layered deposits, thanks to the greater area of gas-water contact. A relatively high hydrate content in

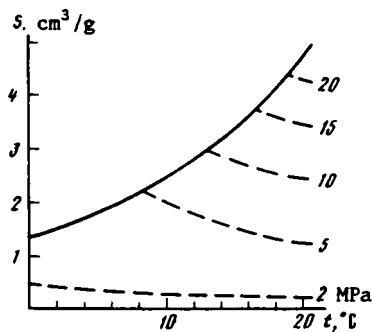


Fig. 1. Solubility of methane S in dependence on temperature [18] in equilibrium with hydrate (solid line) and solubility isobars (dashed lines).

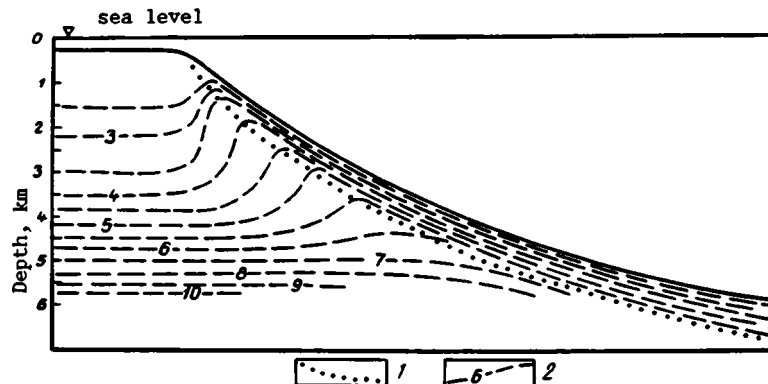


Fig. 2. Methane solubility in pure water for P-T conditions of continental margin depths. 1) Bottom of the zone of methane hydrate stability; 2) isolines of methane solubility in pure water, cm^3/g . Data on solubility is adopted from [18, 20]. Assumed: floor temperature for water depth up to 500 m $+5^\circ\text{C}$, for greater depth $+2^\circ\text{C}$; geothermal gradient of 30 deg/km; hydrobaric gradient 10 kPa/m.

the reservoir is more probably near this contact. In the case of complete replacement of gas, hydrate and water will exist in the deposit. The layer pressure falls in the course of hydrate formation; some decrease in the number of deposits and their water depletion is possible.

The possibility of separating hydrates from a solution of gas in water is determined by the solubility characteristics of gases in equilibrium with hydrates. The point is that the pressure of dissolved gas in such conditions is limited not by the external pressure, but by the equilibrium pressure of hydrate formation for a given temperature [2]. Since the equilibrium pressure lessens with lowered temperature, the solubility of gas in water also decreases (Fig. 1). We note that this tendency is contrary to the known increase of solubility with lowered temperature under normal conditions (when hydrate formation is impossible) [20]. Thus, for cooling of gas saturated water in equilibrium with hydrate, this quantity will grow due to the decrease of gas solubility. So if 1 g of water saturated with methane for 20°C and pressure of 10 MPa, is cooled to 2°C , then its gas content due to hydrate formation is decreased 40% of its initial value,* to 1 cm^3 (see Fig. 1)†. But the quantity of water converting into hydrate decreases insignificantly, in all by 0.5%. In conditions at depth the forming hydrate occupies 0.5% of the rock's pore volume.

*Here and further, gas volume is cited for normal conditions.

†In connection with the preliminary character of the calculations, here and further we disregard the effect of water salinity on gas solubility; the possible error due to this does not exceed 20%.

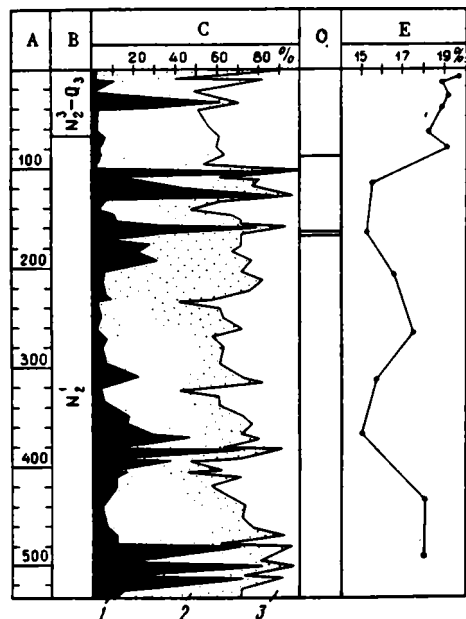


Fig. 3. Lithologic and hydrogeochemical control of the appearance of gas hydrates in a section of deep water drilling well 491 (Pacific coast of Mexico) [36, 44]. A) Subfloor depth, m; B) stratigraphic age; C) granulometry of grains (fractions: 1) sand; 2) silt; 3) clay; D) appearance of hydrates; E) chlorine content of pore waters, ‰.

Calculations show that for the natural process of cooling at depth connected with formation of the cryolithozone, the above cited estimate is close to the maximum possible, even if we take a cryolithozone thickness equal to 1000 m, and a temperature decrease in the sub-glacial part of the section as quasi-stationary. It is evident that hydrates forming from water saturated gas in the framework of the cryogenetic model will be found in a dispersed state in the rock, that is, they will not form accumulations. It is necessary to note that limiting gas saturation of underground waters in regions where cryogenesis is developed seldom occurs.

We will return now to systems in which gas hydrate is formed from ice. It is evident that this is possible for the transition of the gas + water or gas dissolved in water cooling system across the freezing point, and that since in most of these systems up to water freezing, formation of hydrates in accumulations (not dispersed) is practical only in the first case. Hydrate formation by freezing water contributes to cryogenic pressure [30].

Cryogenic gas hydrates may be detected both on land and on water regions: on polar shelves. The conditions for their formation were created on shelves in periods of subareal development, when the growing thickness of the cryolithozone reached 300 m [7].

From the discussion it is clear that cryogenic hydrates may form more or less large accumulations only in association with earlier existing gas deposits. However up to the present time not a single gas deposit with uniquely identified hydrates has been known. Hydrates in gas bearing reservoirs are only conjectured from non-uniquely interpreted well-logging data and by other signs, which also permit different interpretations.

This also concerns the known Messoyakhsk occurrence. Cryogenic hydrates may not be considered for a predicted estimate of the geologic resources of crude hydrocarbon, since the gas in them is not an "addition" to resources of "normal" gas (considered by one or another cited methods), and forms its fraction. But extraction of this fraction presents a significant problem and it is therefore necessary to explain for an estimate of extracted resources.

Compression. Conditions for hydrate formation in a system of free gas + water may be caused by its compression - if the gas in it is greater than necessary for water saturation by increased pressure, for example, in gas deposits forming on land or on shelves and appearing with deeper water conditions. We will term this model *transgressional*. Deposits corresponding to it are almost unknown. Hydrate formation in gas deposits under compression conditions is analogous to the cryogenic model: in some cases a decrease in their size and water depletion are possible. In resource plan both models are identical.

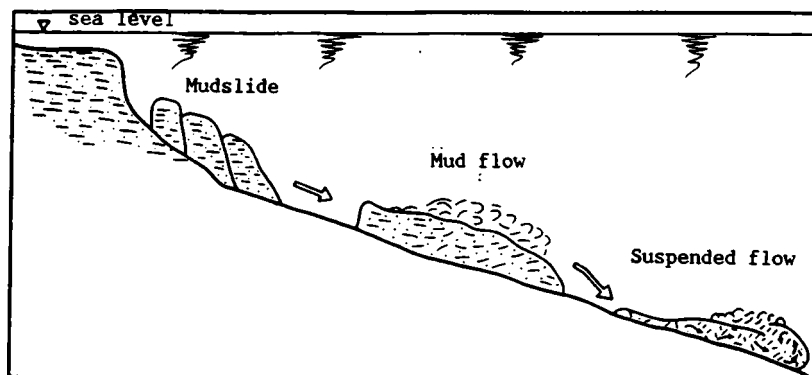


Fig. 4. Model of gravitational flows of sedimentary material on the continental slope (after [46] with minor alterations).

It is not possible to form hydrates from water saturated gas for conditions of external pressure. Hydrate formation due to cryogenic pressure for freezing water is described above, in discussion of the cryogenetic model.

Growth of Concentration. Apparently the growth of water concentration could not exert influence on gas hydrate formation in the earth's crust (although this effect takes place by itself, e.g., in mineral dehydration). We will consider the increase of gas concentration. At depths it may occur by diagenesis. In a submarine environment where the temperature permits the existence of hydrates, if the quantity of authigenic biochemical gas dissolved in pore water increases enough that its pressure reaches the equilibrium pressure of hydrate formation, then hydrate precipitation begins in the pores. We will term this the *diagenetic* model. Its analysis is very important for the problem of gas hydrate geology, since it is considered that thus significant gas resources are formed in the depths of the oceans [25, 26, 28, 29].

Diagenetic transformation of marine sediments, and in particular biochemical gas formation, have not yet been investigated to such a degree that a quantitative model of hydrate genesis could be constructed. The role of various reactions has been discussed, and their rates have been somewhat investigated [5, 34, 42], but there is no clarity in the estimates of organic material consumption in these reactions. It is also necessary to note that diagenetic processes were basically studied under shelf conditions, while hydrates may originate mainly in deep water.

It is however generally accepted that vertical zonality of early diagenetic oxidation–reduction reactions exists, and that methanogenesis occupies a defined place in them. Methane formation begins at some depth below the floor, where the concentration of sulfate-ion is sufficiently decreased in the pore water (by more than 80% in comparison to marine water). This depth generally varies from 0.2 to 200 m [34], but may reach even 600 m [5, 41]. It is considered to depend mainly on the rate of sediment accumulation and the content of organic material in the sediment [34], while dependence in both cases is the reverse. It is known that both of the controlling indicators are characterized by circumcontinental zonality [15, 27]. In agreement with data [33], for low C_{org} (less than 5%), microbial methane cannot form at all. Higher values are inherent to the periphery of oceans and are not peculiar to its inner regions [27].

A kinetic model of diagenetic gas hydrate formation should consider the rates of several processes, with methanogenesis first. In actual conditions, a portion of the gas being generated is inevitably dispersed, diffusing in the direction of the floor, and therefore the rate of hydrate formation is certainly less than the rate of methane generation. As a result of the transformation of part of the pore water into hydrate, the salinity of the remaining water increases. The pressure of the dissolved gas increases in equilibrium with the more saline water. Therefore, in order that the process continue, the rate of methane generation should be greater. At the same time, the salts which are concentrating in the pore water, as well as gas, will diffuse from the reaction zone. The thermal balance of the developing processes is also significant, since hydrate formation is an exothermic reaction. Finally, one of the basis diagenetic phenomena is the lithification of sediment. It is understood that the occupation of pres by hydrates will be more effective if intensive dehydration precedes methanogenesis, and vice versa. Creation of a model which considers all of the processes is an extremely difficult problem, and we will consider only in most general outline the limitations with the aspect of the rate of methanogenesis.

In order that the first portion of hydrates separate from pore water occurring at a temperature of 3–4°C, it should contain 1.5–1.7 cm³/g of methane (see Fig. 1). If gas generation continues for 10 thousand years, the its rate

should be no less than $(2.3-2.7) \cdot 10^{-12} \text{ cm}^3/\text{cm}^3\text{-sec}$ (in calculations on water saturated rock, for a porosity of nearly 50%). For a duration of 10^5 years the rate may be an order smaller. Burial under sequence of accumulating deposits was accompanied by the heating of pore water due to deep heat flow. At a higher temperature, a greater gas content of the water is required for hydrate formation: for 10°C : 2.5 g/cm^3 ; for 20°C : $4.5 \text{ cm}^3/\text{g}$ (see Fig. 1).

We note that each rate of methanogenesis is necessary in these conditions, in order to secure continuation of earlier starting hydrate accumulation. For this we define geothermal gradient values of 50 deg/km , and sediment accumulation rates of $100 \text{ cm}/1000 \text{ years}$. These are probably close to maximum for the oceans beyond the shelf limits. The increase indicates that on the interval of temperature growth from 3 to 10°C , methane should be generated in the rock with an average rate no less than $1.3 \cdot 10^{-13} \text{ cm}^3/\text{cm}^3\text{-sec}$, and on the interval $10-20^\circ\text{C}$, no less than $2.6 \cdot 10^{-13} \text{ cm}^3/\text{cm}^3\text{-sec}$. From microprobe data [1, 3, 21, 22], rates of biochemical methane formation in marine sedimentary deposits of various regions generally reach a magnitude on the order of $10^{-13} \text{ cm}^3/\text{cm}^3\text{-sec}$, sometimes increasing by one order and sometimes by two orders. In light of these data, hydrate formation in the framework of the diagenetic model is realized in principal in deposits of the more ancient Holocene.

Another question arises: is it possible for rock to have a high content of gas hydrates which are forming in conformity with the given model? This depends on the quantity of the initial material, organic carbon, which transformed into hydrate. It is possible to calculate, e.g., that for filling by hydrates half the pore volume in a rock which possesses a porosity of 50%, it is necessary to "rework" without loss a quantity of carbon exceeding 2% of the mass of the mineral part of the rock. Organic carbon contents of this order in bottom sediments of the global ocean occur only on its periphery, and far from generally [22].

On the basis of the discussion it is possible to conclude with high probability that formation of hydrates in the framework of the diagenetic model did not lead to significant hydrate content in the rocks. Dispersed hydrates of such genesis (with content in single percents) may be occur in peripheral regions of the ocean (beyond the shelf limits), in deposits of the more ancient Holocene enriched by original material, and at some depth below the floor: below the sulfate reduction zone.

Observational materials on gas hydrates in deposits of the global ocean indicate their possible formation from biochemical gas. this is indicated by a comparatively high content of organic carbon in hydrate-containing deposits [11], and the isotopic composition of carbon in the gases [4]. In addition, as a rule, there is a correlation of hydrates to voids, fractures, or relatively permeable horizons [11]. This attests to the formation of hydrates from moving fluids, and not from gas generated in situ, that is, at variance with diagenetic model.

From data of investigation into hydrate phenomena on the underwater Blake outer ridge in the Northwest Atlantic, which based on isotope data, was formed by biochemical gas [4] and correlated to deposits that are relatively rich in organic carbon (C_{org} 1.1-2.4%) [31], on the basis of isotope data a balance calculation was carried out on the intensity of methane genesis in the section [35]. The calculation was performed suitably for conditions corresponding to the diagenetic model of hydrate formation in our understanding. As a result it was shown that the calculated quantity of generated methane is insufficient for saturation of pore waters and precipitation of hydrates from them. This result, in the opinion of the authors [35], contrasts with observations, but the inconsistency may be removed, in particular, by application of another model of hydrate formation. Hydrate formation in a system of biochemical gas in situ + ice, may probably take place in tundras, however the geologic value of such hydrates is scarcely great.

We will proceed to *dynamic systems*. We recall that we understand them to be a system in which gas hydrates are formed as a result of the transport of material into the reaction zone. It is possible to describe four methods of transport: filtration, molecular diffusion, transport of reagents in the course of fluidization of rocks, and displacement of blocks of rocks.

Filtration. Hydrates may be deposited in reservoirs by filtration of gas and gas saturated water. We will first consider the latter case.

It is evident that filtering gas saturated water, reaching zones of hydrate stability, is indicated by supersaturated gas (by virtue of the decrease in its solubility, see Fig. 1) and it becomes the hydrate source. Apparently, the most widely distributed natural variety of regional filtration of gas saturated waters are elisional flows, which are characteristic for buried forming sedimentary rock basins. If such a basin lies on a contemporary continental margin, and some part of it lies within the limits of deep water, gas hydrates will be accumulated in that part from waters which are filtering into the ocean. This is the elisional model of hydrate formation. The effectiveness of the elisional model is determined in particular by the deep cooling at the depths of continental slopes

and slope feet in comparison with the adjacent shelf and land, as a result of which the variation in gas solubility at one or another absolute depth may reach several cubic centimeters per gram (Fig. 2).

Water filtration may be ascending, especially lateral, or emerging. In every case on its path to submarine discharge it will leave hydrates in the reservoirs. The dissolved gas which forms hydrates in the given model may be also diagenetic and catagenetic. It is most likely that a significant part of the hydrate appearances detected in the Pacific and Atlantic oceans [38] represents hydrates forming in agreement with the given model. It was already mentioned above that the hydrates in them are correlated with voids, fractures, and relatively permeable horizons.

Thus, hydrates detected in a core of deep water drilling well 491 in the Central American trough, judging by granulometric composition, are controlled by the relatively good permeability of the horizon on the interval of subfloor depth of 100–200 m (Fig. 3). An anomaly of pore water composition is observed on this horizon. It is expressed by a decrease in salinity and chlorine. From seismic investigation data [44], this horizon, as well as all hydrate displacing sequences, was accumulated to the side of dry land. It is more likely that the hydrates in the given case were formed from underground waters which were filtering to the side of the ocean.

It is probable that hydrates of elisional genesis are connected with the reflecting seismic horizon BSR (bottom simulating reflector) widely distributed on continental slopes. This reflector intersects sedimentary layering and is interpreted as the bottom of the hydrate bearing zone [43]. Such a horizon is also observed in a portion of well 491 [44].

The path to an estimate of the distribution scales of gas hydrates forming in agreement with the elisional model lies through calculations of the quantity and gas content of the waters squeezed out from the sedimentary-rock basin into the ocean during the existence of the necessary thermo-baric conditions. Subduction stress has a definite role in squeezing of the waters on active continental margins, and features of the geothermal regime are important in gas generation.

Heating by a local source (magmatic chamber, intrusion cooling) may be the cause of underground water filtration. Convection hydrothermal systems are known to form under the influence of this heating. If sedimentary rocks with sufficient thickness an organic material content appear in the sphere of influence of such a system, hydrocarbon gas generation becomes possible in them. When filtering water with dissolved gas reaches the zone of hydrate stability, they begin to precipitate in the case of sufficiently high gas content in the waters. This is the *hydrothermal* model of gas hydrate formation. A hydrate accumulation detected in the Sea of Okhotsk in the place of an anticipated hydrotherm was probably formed in the discharge zone of methane bearing thermal waters [13]. It is possible to propose from seismic exploration data [40] that hydrates in the Guaymas basin (Gulf of California) may have a similar genesis.

Hydrate formation from filtering of gas saturated waters is possible in principal on land and on shelves in regions with a thick cryolithozone. However, this process is hardly widely developed, since a deficit of layer pressure forms as a result of cryogenic cooling in water pressured systems, and movement of deep waters to the surface does not occur under these conditions [8].

Filtration (or string migration) of gas, as is known, occurs under the influence of buoyancy force and requires the preliminary formation of an accumulation of some height sufficient for overcoming resistance to buoyancy.

It is possible to represent the mechanism for separating hydrates in the pores of filtering gas of the reservoir by the following example. At the moment of entry of a string of gas into the zone of hydrate stability, a hydrate film forms on the frontal part of the string (in the pores) on the gas–water boundary. If the power of buoyancy proves insufficient for "breaking open" this film the gas will flow around it. If the film is broken through, the string is propelled upwards by the flow. But formation of hydrate from this portion is inhibited in connection with the presence of the film and with the increasing salinity of the remnant water in the hydrate bearing reservoir. The gas of the string's frontal part which is propelled by the flow falls under conditions analogous to initial conditions, and the new part of this gas is precipitated in pores in the form of hydrate. The result of this process is the "smearing" of the filtering gas string.

At the same time it is necessary to give attention to the possibility of "straight-through hydrate" gas filtration. The effect evidently depends on the sizes of the gas string, the filtration pressure, the permeability of the reservoir and the hydrate film, the layer water salinity, and the possibility of diffusional dispersion of salts concentrating as a result of hydrate formation. It is possible to judge that "straight-through hydrate" filtration actually occurs from the numerous observations of long-time active gas gryphons in the neighborhoods of shut-down gas wells located in re-

gions with a thick cryolithozone. This is indicated by an interlayer return flow of gas which accompanies hydrate formation in the near-well reservoir zone in the Messoyakhsk occurrence [12].

The described *string-migrational* model of gas hydrate formation may be realized in various geologic conditions: in sediment-rock basins which are undergoing burial, when the gas is separated from elisional flows of underground waters; in uplifting regions, when the cause of gas separation is the decrease of layer pressures; and in stages of relative hydrodynamic rest, in the course of oscillating and structure forming tectonic motions, in the retransformation of gas deposits. Such conditions may be in different oil and gas bearing basins: on land or aquatic.

Submarine hydrates formed from free gas, which was separated from elisional water flows even outside the zone of hydrate formation are hardly feasible, and are possibly distinct from hydrates directly deposited by the water of these flows. Both types must be rationally considered in the elisional model. Hydrates formed by strings of supernatant gas in regions with a thick cryolithozone are another matter. They may be deposited in zones of gas accumulation on the slopes of positive structures of various order, and on monoclines immediately under regional and local cover in the form of more or less concentrated accumulations. If they lie in immediate proximity to gas deposits, then the gas resources contained in them may present interest, since at least a portion of these resources may be recovered by working of these deposits (as attracted reserves). Such accumulations have not occurred up to this time.

Formation of natural hydrates in a gas-hydrate filtering system has probably not played a significant geological role on account of the lower gas permeability of frozen rocks.

Summing up the considered filtering models we turn our attention to the principal distinctions of the effectiveness in hydrate formation by filtration of gas saturated water and filtration of gas: in the first case, gas concentration occurs, and in the second, depletion. In fact the concentration of gas in hydrate is always greater than in a water solution, and is certainly less than in a single phase gas system. The elimination of salts concentrating in the water directly in the course of filtration is also a distinguishing feature in the separation of hydrates from the filtering water solution (in comparison with gas). Until the necessary thermobaric conditions exist, until water filtration is continued, and until this water is gas saturated, nothing will interfere in the precipitation of hydrates from solution. The accumulation of hydrates in filtering reservoirs is an important feature of such models.

In conclusion we will turn our attention to two gas-geochemical features of the filtration model. The first feature is the chromatographic effect which is caused by the differing capacities of natural gas components to form hydrates: the composition of the gas in the hydrates should vary in the direction of filtration. such an effect is intrinsic to all filtration models. The second feature is characteristic for an elisional model under continental slope conditions. The thickness of the zone of hydrate stability on the slope is considered dependent mainly on the thermobaric environment. But it may also vary as a result of regular variation (caused by depth) in the gas composition in the oil and gas bearing basin: gas should be different in fluids filtering into ocean at different levels of the continental slope.

Molecular diffusion. In the oil and gas geological literature diffusion is mainly considered as a mechanism for the dispersion of hydrocarbon accumulations. However in conditions when underground waters in the whole volume of the system are saturated by hydrocarbons, and a gradient of concentration exists caused by a gradient of solubility, it seems that diffusion may play a role in the initial migration and initial accumulation of hydrocarbons [6, 23]. In this sense the geozone of hydrate stability possesses defined specific properties: here the gradients of concentration and pressure of the dissolved hydrocarbon gases may appear significantly greater than in the nonhydrate part of section (see Fig. 1).

In conditions when hydrates could not exist, for a normal hydrobaric gradient, the limiting vertical gradient of pressure in water saturated gas reaches nearly 10 kPa/m, and in the zone of hydrate stability it may reach 100 kPa/m. The greatest values are characteristic for the lower part of this zone. This serves the prerequisite for its type of accelerated diffused "distillation" of gas ("recommendation" in the terminology of [6]) in the hydrate formation zone. However, there is evidently no independent value of diffusion in hydrate formation (in every case in their accumulations).

Displacement in Fluidized Rock Flow. It is possible to name two geological phenomena in which fluidized rocks take part that may be responsible for the formation of hydrates: submarine mud volcanism and the movement of submarine gravitational sedimentational flows. We will term the corresponding models of hydrate formation the mud-volcano-like and the sedimentational.

The *mud-volcano-like* model is characterized by an example of a hydrate appearance in the Southern Caspian [10]. The area of the investigated accumulation (nearly 0.3 km²) was controlled by the crater field of a volcano.

Hydrates have already been detected directly on the floor. It is evident that their stability is secured by moving fluid: gas or gas saturated water. Hydrate content in clay breccia reached 35%. Hydrate inclusions up to 5 cm in size had various forms (often subisometric), and larger but finer layered deposits also occurred.

Similar types of accumulations are detected and investigated in the Black Sea [14] and probably in the Gulf of Mexico [32]. Apparently, subisometric aggregates of hydrates are formed as a result of the bubbling of bubbly gas in diluted clay breccia, while layered aggregates formed by the motion of fluids in fractures.

Underwater mud-volcano gas hydrates are evidently correlated to regions with thick young sedimentary cover which are undergoing rapid burial. Thanks to shallow deposition such accumulations present a favorable object for the study of submarine gas hydrate formation. The genetics of this model are close to the elisional model.

The idea of the *sedimentational* model was introduced by solving the nature of the most effective of all known hydrate appearances: an almost monomineralic hydrate body nearly 4 m thick which was discovered in deep sea drilling well 570 on the inner slope of the Central American trench [9]. At the base of this model lie representatives of avalanche sedimentation [16], in particular gravitational flows transporting sedimentary material from the first global level of sediment accumulation (the sea—river boundary) to the second (the base of the continental slope), or, on active continental margins, to the third (the floor of the deep water trench).

Gravitational flows are a sequence characterized by the dilution of sedimentary material by water in proportion to movement along a slope. At the start of this sequence are underwater landslides and avalanches, and gravities of other classes are formed from them (Fig. 4). Massive rocks drawn into the displacement may contain free gas that is entrapped in pores or in accumulations in their initial deposition. This gas on one hand is entrained downwards by the moving flow, and on the other, releasing and coalescing in proportion to dilution of the flow, it is rushing towards the surface. It appears that in deep water thermobaric conditions, the gas transforms to hydrate, causing "gelling" of the flow which contains it.

Experimental investigations on gas bubbles which are floating in opposition to the flow showed that the hydrate layer on the bubble boundary is formed rapidly, even if there is no dissolved gas in the water [45]. After formation of the hydrate layer the buoyancy rate of the bubbles is sharply slowed, which is explained by the high density of hydrate in comparison to gas [39]. A gas bubble coated by hydrate moving in a flow of gravities will evidently be crushed as a result of growth of external pressure, and all of the gas of the bubble will transform into hydrate.

Hydrates forming in agreement with the given model will be dissolved in sea water; necessary conditions for the preservation are rapid burial under a sequence of gravities and high hydrate content. The quantity of sedimentogenic hydrates in gravity bodies is determined by the sizes of the avalanche massifs, their initial gas content, and the hydrodynamic conditions of the material's transport and deposition; it is evident formation of different bodies is possible, ranging from almost monomineralic bodies, similar to that detected in well 570, to scarce fine inclusions. Formation of sedimentogenic gas hydrates is most probable on steep continental slopes with developed gravitational tectonics, adjacent to wide shelves or paleoshelves with gas bearing sedimentary cover.

Displacement of Blocks of Rocks. It is possible for one to propose the dropping by means of faulting of a large block of rock which contains a gas deposit, from the land or shelf into a relatively deep water environment, without destruction of its layering. Such a fault model is in effect completely analogous to the transgressional model. Such hydrates have not been observed.

Thus, sorting of possible physical mechanisms for gas hydrate genesis made it possible to distinguish several geological models for this process. They are distinguished by the degree of satisfaction of theoretical considerations, by the materials of observation, and mainly by their results. Gas concentration occurs for hydrate formation in agreement with the elisional, hydrothermal, underwater mud volcanic, diagenetic, and (for defined conditions) sedimentational models. Hydrate accumulation and formation of their aggregates is completely probable within the limits of the first three models.

Hydrate accumulations of sedimentational genesis are also possible, but they are formed instantaneously, in a geologic sense. Formation of concentrated diagenetic accumulations of hydrates is improbable; dispersed hydrates of this genesis may occur in pre-Holocene deposits in conditions of high organic material content and a large rate of methanogenesis.

All of these models may be realized in submarine conditions, on continental slopes, slope feet, and in deep water inner seas within the limits of sedimentary-rock basins with rapidly forming sedimentary cover. Accumulations formed adequately by the elisional, hydrothermal, underwater mud volcanic, and sedimentational models may have resource values.

In regions with a thick cryolithozone (on land and polar shelves), hydrate accumulations may be formed in agreement with the cryogenetic and string migrational models; gas depletion occurs in both cases. In the cryogenetic model, hydrate accumulations are connected with earlier existing gas deposits; the presence of hydrates decreases the fraction of the reserves extracted from them. Gas resources concentrated in accumulations of string-migrational genesis may have practical interest.

LITERATURE CITED

1. F. A. Alekseev, G. I. Voitov, V. S. Lebedev, and Z. N. Nesmelova, Methane [in Russian], Nedra, Moscow (1978).
2. E. S. Barkan and A. N. Voronov, "Estimates of gas resources in zones of possible hydrate formation," *Sov. Geol.*, No. 8, 26-29 (1983).
3. S. S. Belyaev, "Microbiological methane formation in different ecosystems," in: *The Role of Microorganisms in Gas Cycles in Nature* [in Russian], Nauka, Moscow (1979), pp. 205-219.
4. É. M. Galimov and K. A. Kvenvolden, "Geochemistry of gases in gas hydrate containing deposits of the Blake outer ridge region (Atlantic ocean)," *Geokhimiya*, No. 7, 1075-1983 (1979).
5. É. M. Galimov and K. A. Kvenvolden, *Investigations of Organic Material in Gases and Sedimentary Sequences of the Floor of the Global Ocean* [in Russian], Nauka, Moscow (1982).
6. A. A. Geodekyan and A. V. Egorov, "Directed diffusional recondensation — a possible mechanism of initial migration," in: *Energy and Mechanism of Initial Hydrocarbon Migration* [in Russian], Nauka, Moscow (1988), pp. 38-43.
7. G. D. Ginsburg, "On the formation of crystallohydrates of natural gases at depth," in: *Hydrogeology of the Eniseisk North* [in Russian], NIIGA, Leningrad (1969), pp. 109-128.
8. G. D. Ginsburg, *Geothermal Conditions and the Oil and Gas Potential of the Noril'sk Region* [in Russian], Nauka, Moscow (1973).
9. G. D. Ginsburg, I. S. Gramberg, I. S. Guliev, et al., "Features of lithogenesis for gas hydrate formation in the depths of the global ocean," *Dokl. Akad. Nauk SSSR*, 288, No. 6, 1446-1449 (1986).
10. G. D. Ginsburg, I. S. Gramberg, I. S. Guliev, et al., "Underwater-gas volcanic type of gas hydrate accumulations," *Dokl. Akad. Nauk SSSR*, 300, No. 2, 416-418 (1988).
11. G. D. Ginsburg, I. S. Gramberg, I. S. Guliev, et al., "Basic genetic types of submarine gas hydrates," in: *Geology of the Seas and Oceans* [in Russian], PGO "Sevmorgeologiya," Moscow (1988), pp. 81-88.
12. G. D. Ginsburg, V. V. Tikhomirov, A. V. Baranov, and A. A. Novozhilov, "Gas composition as a sign of secondary hydrate formation," *Gazo. Prom-stv.*, No. 3, 23-24 (1985).
13. A. P. Zonenshain, "Gas sources on the floor of the Sea of Okhotsk," *Priroda*, No. 8, 53-57 (1985).
14. A. N. Kremlev and G. D. Ginsburg, "First results of the search for submarine gas hydrates in the Black Sea," *Geol. Geofiz.*, No. 4, 110-111 (1989).
15. G. Kukla, *Rates of Geological Processes* [Russian translation], Mir, Moscow (1987).
16. A. P. Lisitsyn, *Avalanche Sedimentation and Interruptions in Sediment Accumulation in Seas and Oceans* [in Russian], Nauka, Moscow (1988).
17. Yu. F. Makogon, "Formation of hydrates in a gas bearing layer under permafrost conditions," *Gazov. Prom-stv.*, No. 5, 14-15 (1965).
18. Yu. F. Makogon and D. V. Dévidson, "Effect of excess pressure on stability of methane hydrate," *Gazov. Prom-stv.*, No. 4, 37-40 (1983).
19. K. B. Mokshantsev and N. V. Cherskii, *Basic Outlines of the Geologic Structure and Prospects of the Oil and Gas Potential of Eastern Yakutiya* [in Russian], Yakut. Kn. Izd-vo., Yakutsk (1961).
20. A. Yu. Namaiot and M. M. Bondareva, *Solubility of Gases in Water Under Pressure* [in Russian], Gostoptekhizdat, Moscow (1963).

21. Oil and Gas Genetic Investigations of the Bulgarian Sector of the Black Sea, Series: Izd. Bulg. Akad. Nauk, 1984.
22. Okeanologiya. Chemistry of the Oceans, Vol. 2, Nauka, Moscow (1979).
23. V. P. Savchenko, "A method of directed searches for gas occurrences," Tr. VNIIGAS, Issue 42/50, 5-55 (1968).
24. V. A. Solov'ev and G. D. Ginsburg, "Geothermal investigations in the global ocean in connection with the study of gas hydrate potential," Litol. Polezn. Iskop., No. 5, 121-125 (1987).
25. A. A. Trofmuk, N. V. Cherskii, and V. P. Tsarev, "Gas hydrates, a new source of hydrocarbons," Prioroda, No. 1, 18-27 (1979).
26. A. A. Trofmuk, N. V. Cherskii, V. P. Tsarev, and S. P. Nikitin, "A means of utilization of gas hydrate deposits," Geol. Geofiz., No. 1, 3-10 (1982).
27. V. Ya. Trotsyuk and M. M. Marina, Organic Carbon in Deposits of the Global Ocean [in Russian], Nauka, Moscow (1988).
28. N. V. Cherskii and V. P. Tsarev, "Estimates of resources and several questions on the prospecting and extraction of natural gases from sediments of the floor of the global ocean," Geol. Geofiz., No. 5, 22-31 (1977).
29. N. V. Cherskii, V. P. Tsarev, and S. P. Nikitin, Investigation and Prediction of the Accumulation Conditions of Gas Resources in Gas Hydrate Deposits [in Russian], YaF SO Akad. Nauk SSSR, Yakutsk (1983).
30. V. S. Yakushev, "One of the possible causes of gas emissions in sequences of permafrost rocks," Geol. Nefti Gaza, No. 4, 45-46 (1989).
31. J. M. Brooks, L. A. Barnard, D. A. Wiesenburg, et al., "Molecular and isotopic composition of hydrocarbons at site 533, DSDP Leg 76," Initial Reports of DSDP, Wash., 76, 377-389 (1983).
32. J. M. Brooks, H. B. Cox, W. R. Bryant, et al., "Association of gas hydrates and oil seepage in the Gulf of Mexico," Org. Geochem., 10, 221-234 (1986).
33. G. E. Claypool and I. R. Kaplan, "The origin and distribution of methane in marine sediments," in: Natural Gas in Marine Sediments, Plenum Press, New York (1974), pp. 94-129.
34. G. E. Claypool and K. A. Kvenvolden, "Methane and other hydrocarbon gases in marine sediments," Ann. Rev. Earth. Planet. Sci., 11, 299-327 (1983).
35. G. E. Claypool and C. N. Threlkeld, "Anoxic diagenesis and methane generation in sediments of the Blake outer ridge, DSDP site 533, Leg 76," Initial Reports of DSDP, Wash., 76, 391-402 (1983).
36. J. M. Gieskes, K. Johnston, and M. Boehm, "Appendix. Interstitial water studies. Leg 66," Initial Reports of DSDP, Wash., 84, 961-967 (1985).
37. R. Hesse and W. Harrison, "Gas hydrates (clathrates) causing pore-water freshening and oxygen isotope fractionation in deep-water sedimentary sections of terrigenous continental margins," Earth and Planet. Sci. Lett., 55, No. 3, 453-462, (1981).
38. K. A. Kvenvolden, "Methane hydrate — a major reservoir of carbon in the shallow geosphere?" Chem. Geol., 71, 41-51 (1988).
39. B. B. Maini and P. R. Bishnoi, "Experimental investigations of hydrate formation behavior of a natural gas bubble in a simulated deep sea environment," Chem. Eng. Sci., 36, 183-189 (1981).
40. R. Merewether, M. S. Olsson, and P. Lonsdale, "Acoustically detected hydrocarbon plumes rising from 2 km depths in Guaymas Basin, Gulf of California," J. Geophys. Res., 90, No. B4, 3075-3085 (1985).
41. R. S. Miller, J. M. Lawrence, and J. M. Gieskis, "Interstitial water studies. Sites 386 and 387, Leg 43," Initial Reports of DSDP, Wash., 43, 669-674 (1979).
42. W. S. Reeburgh, "Rates of biochemical processes in anoxic sediments," Ann. Rev. Earth. Planet Sci., 11, 269-298 (1983).
43. T. H. Shipley, M. N. Houston, and R. I. Buffler, "Seismic evidence for widespread possible gas-hydrate horizons on continental slope and rise," Bull. AAPG, 63, No. 12, 2204-2213 (1979).
44. Site 491, Shipboard Sci. Party, Initial Reports of DSDP, Wash., 66, 219-232 (1982).
45. D. R. Topham and P. R. Bishnoi, "Deep water blowouts," Spill Technol. Newslett., 5, No. 3, 88-94 (1980).
46. R. Wright and J. B. Anderson, "The importance of sediment gravity flow to sediment transport and sorting in a glacial marine environment: Eastern Weddell Sea, Antarctica," Bull. Geol. Soc. America, 93, 951-963 (1982).

STROMATOLITIC NATURE OF SILICEOUS HORIZON IN THE CHULAKTAUSK SUITE OF MALYI KARATAU

T. V. Litvinova

UDC 553.64:552.55(574.1)

Stromatolitic structures developed in siliceous deposits of the Vendian Chichkanssk Suite are compared with stromatolitic forms distributed through the Lower Cambrian Chulaktausk Suite of Malyi Karatau. A widely distributed biogenic fabric is demonstrated in a phosphorite-bearing succession of this basin.

Many studies have recognized the essential role of biogenesis in the formation of siliceous horizons in the Chulaktausk Suite of Malyi Karatau. Kholodov [18] emphasized the planktonic contribution to the development of phthanite, which is deposited in relatively deep-water areas. Tabyldiev and Cherbyanova [16] noted that during the first half of the period, considerable accumulation of siliceous sediment was caused by sponges assisted, in the opinion of the authors, by the quiet sedimentary environment of the Cambrian basin. Eganov [6] considers, following a detailed investigation of the siliceous horizon in Malyi Karatau, that it is possible to recognize a large number of diverse biohermal fabrics, which can often only be distinguished with difficulty. This is due to the extensive and very irregular recrystallization, which is affected by the original lithology, bed thickness, postsedimentary stresses, and the numerous brecciated layers described in [19] in relation to the Dzhanil phosphate deposit. These cause difficulties not only in studying, but even in identifying biogenic structures, which are often mistaken for sedimentary features.

Before passing to the main point of interest, a brief summary of the geological structure of Malyi Karatau will be given. It consists of Riphean, Vendian, Cambrian, and Ordovician deposits divided into five series: the Kondzhotsk, Bol'shekaraisk, Zhanatassk, Malokaraisk, and Tamdinsk.

The Kondzhotsk Series (exposed thickness 3000 m) is the oldest in Malyi Karatau. It is composed of metamorphic rocks, including talc-chlorite-sericite schists, quartzites, phyllites, and limestones, with crushed zones and isoclinal folding. Most workers place it in the Middle Riphean. The Bol'shekaraisk Series (2060 m thick) is composed of polymict sandstones, clay-slates, siltstones, and phyllites. The Zhanatassk Series (3000 m thick) comprises microphytal limestones with interbeds and lenses of red chemical limestones. The Malokaraisk Series (2000-3000 m thick) is subdivided into four suites; the Koksuisk (argillites, siltstones, granule and pebble conglomerates), Aktugasik (arkosic and polymict sandstones), Chichkanssk (phthanites, shales), and Kurgansk (tuffites, tuffaceous sandstones, and shales). The Tamdinsk Series is divided into three unequal suites; the Kyrshabaktinsk, the productive Chulaktausk, and the carbonate-rich Shabaktinsk. The thickness of the latter may reach 4500 m. The Kyrshabaktinsk Suite is composed of tuffaceous blocks, cemented in a carbonate-clayey sandstone mass. Red-colored rocks in this suite are impersistent both laterally and vertically (0-150 m).

Several horizons can be distinguished within the Chulaktausk Suite. The "lower" dolomite horizon is found at the base, and occurs virtually everywhere. Brodskaya and Kholodov [1] proposed a reefal origin for the "lower" dolomite in 1965. Where the exposure of this phosphate-bearing deposit is sufficient (Dzhanil, Degeres etc.), it is seen to be composed of a series of bioherms. These each have a thickness of around 12 m at the center, decreasing to 8-10 m around the margins. The length of each bioherm is usually around 15-16 m. Each phosphate occurrence displays a similar thickness variation, and has an irregular top surface formed of rounded domes and hollows. These are apparently related to the form of biohermal growth. The "lower" dolomite horizon is overlain by a siliceous horizon, in which spongiolites, phthanites, siliceous-argillaceous shales, and chert (chalcedonolites) can be distinguished [4]. The structure and composition of the phosphatic horizon above has been the subject of numerous papers [2, 3-5, 16, 17, et al.]. It is usually composed of one, two or three phosphatic bodies, separated by siliceous-carbonate-argilla-

ceous shales, but it may be differentiated into a rhythmically-interbedded sequence of phosphorites and phosphate-carbonate-argillaceous shales.

The topmost section of the Chulaktausk Suite is an iron-magnesium horizon composed of dolomites shot through with iron and manganese. This horizon is rich in oncolites, and chiolites occur. A wavy-banded texture, emphasized by the distribution of manganese, demonstrates the role played by stromatolites in the sedimentation of the dolomites. Despite the limited thickness (0.2-2 m) of this iron- and magnesium-bearing dolomite horizon, it can be recognized virtually everywhere. However, it displays extreme lateral variability, even within a single ore body, and forms a series of lenses with a maximum extent of 15-16 m.

The Chichkanssk Suite of the Malokaroisk Series is separated from the Chulaktausk by two suites: the tuffaceous Kuransk, and the tillite-like Kyrshabaktinsk. A large number of diverse stromatolitic structures are exposed in the Chichkanssk Suite of Malyi Karatau [7]. These have been determined by Kyrlov [9] as *Conophyton gaubitzia*, *Linellaavis* Kryl., and stromatolites with affinities to *Patomia* (more precise definition is prevented by their poor preservation). Stromatolites were encountered in the Chichkanssk Suite in almost all the river valley sections (from the River Uchbas in the West to the River Koktal in the East [9]. A stromatolitic section was described from this suite in the valley of the River Koksuy by Korolev in 1963, and in the same year Maksumova described a section on River Taldybulak (a tributary of the River Chabakty), 3 km from Aktugai.

Detailed lithological studies undertaken by us on a series of phosphate bodies in Malyi Karatau have revealed characteristic textures in the rocks of the siliceous horizon of the Chulaktausk Suite which resemble stromatolitic structures. This prompted us to attempt to analyze undisputed stromatolitic structures in the Chichkanssk Suite, and similar biogenic textures in the Chulaktausk Suite. The most suitable target for this study appeared to us to be at Ayusakkan on the River Chabakty, where on one bank some distinct and excellently preserved stromatolitic structures are visible in the Chichkanssk Suite, whereas on the other bank is a thick and well-exposed section of the Dzhanil phosphatic ore body in the siliceous horizon.

The following types of phthanite succession in the Chichkanssk Suite may be distinguished on the basis of stromatolitic structure (from the base upwards):

Bedded Stromatolites. These are composed of masses of phthanite, practically indistinguishable from the Chulaktausk phthanites. At the base and top of the horizon are zones of banded chert (Fig. 1a). Under the microscope, globular chert structures are visible, in which unevenly distributed bands or patches of organic matter, individual quartz grains, and spherulitic chalcedony displaying extinction crosses, are seen. Between the banded cherts are rocks with thin interbeds of phthanite and argillaceous-carbonate material. Analogous banding may be observed in the Chulaktausk cherts (Fig. 1b).

At the base of the siliceous horizon in the Chulaktausk Suite, [5, 6] describe a distinctive "basal phosphorite," composed of thin (0.1-0.4 m) beds. Its thickness grows in the hollows of bioherms in the "lower" dolomite, whereas in the domes it decreases to zero. This bed is characterized by thin phosphatic and siliceous interbeds, with rarer argillaceous-carbonate material (Fig. 1c, d). Under the microscope the "basal" phosphorite is seen to be composed of fine-grained, more rarely pelletal, phosphorite, interbedded with siliceous or siliceous-carbonate lithologies, and with scattered sponge spicules. Rare rounding of beds is striking, with rhythmic bedding related to the cyclical growth of algae. The "basal" phosphorite forms biostromes, which may be observed not only in the Dzhanil, but also in many other phosphatic deposits in Malyi Karatau. The stromatolitic nature of this bed is noted by Eganov [6].

In several places within the lower parts of Chichkanssk Suite, distinctive fabrics with a biogenic character are found. These occur in blocks 50-60 cm across, and apparently covered with hieroglyphs (Fig. 1e). These have a uniform orientation, and are from 2-5 mm long. Irregular inclusions of chert, 8x10 cm in dimension, are also found. They differ in both composition and color from the groundmass of the rock: they are composed of phthanite with a globular structure, with patches of irregularly distributed organic matter. The groundmass is composed of a series of carbonate rocks, which under the microscope are seen to be fine-grained dolomite.

Beds of chert 6 cm thick are exposed in the siliceous horizon of the Chulaktausk Suite. They are packed with sponge spicules up to 1 cm long (Fig. 1f). They stand out in sharp relief on weathered bedding planes. The groundmass of the bed is formed of phthanite with minor crystalline dolomite, individual chalcedony grains, extended lenses (0.1 mm x 0.5 mm) of fine-grained and oolitic phosphate, altered sponge spicules, and accumulations of partly phosphatized spongiolites. Such an interesting bed, with spongiolites visible to the naked eye, is described by us for the first time, although under the microscope (Fig. 1g, h) spongiolites have been studied and described by many workers [4, 5, et al.]. They are quite widely distributed in Malyi Karatau.

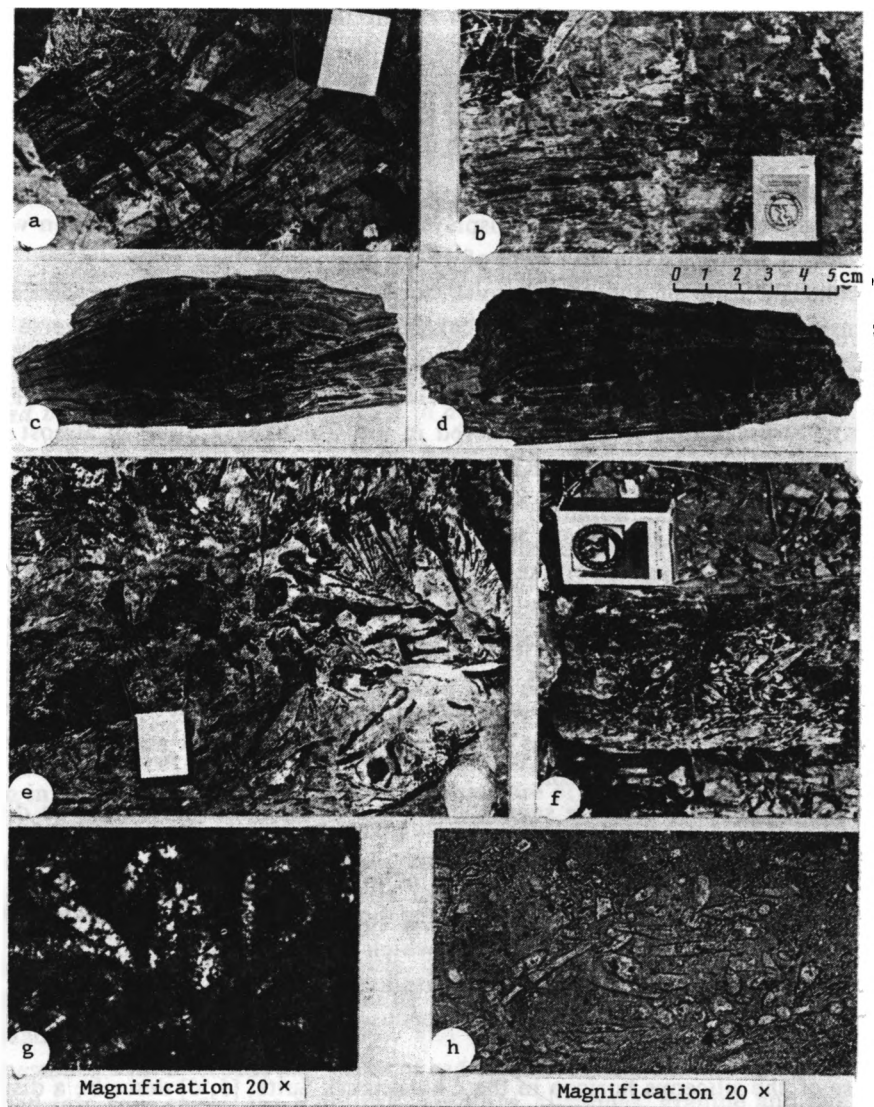


Fig. 1. Bedded stromatolites and spongiolites. a, b) Banding in cherts from the Chichkansk and Chulaktausk Suites respectively; c, d) bedded stromatolites of the Chulaktausk Suite ("basal" phosphorite); e) problematic structures from the Chichkansk Suite; f-h) spongiolites from the Chulaktausk Suite.

Apparently, biostromes occur at the base of the siliceous horizon in the Chulaktausk Suite just as they do at the base of the Chichkansk Suite.

Nodular and Columnar Stromatolites. Several distinctive types of stromatotic structure occur in this horizon.

1. Small rounded mounds (10-30 cm in diameter), formed as though from inflated bands of chert (Fig. 2a). They are seen under the microscope to consist of phthanite with minor crystalline dolomite, and crystals of ore minerals. Similar forms occur in the Chulaktausk Suite (Fig. 2b), where they are also composed of phthanite.

2. Stromatolitic columns, which are generally composed of several blocks 1.2 x 2-3 m in size. In favorable cross sections of columns it is apparent that the rock is rich in "thecae" or "cells," names given to dark, rounded forms composed of phthanite. The groundmass is composed of fine-grained dolomite. The carbonate rock has suffered intense weathering, permitting the "thecae" to be distinguished not only by their color, but also by their relief. In the Chulaktausk cherts, similar biogenic forms (Fig. 2d) are less pronounced, since they are composed mainly of phthanite. The groundmass contains only a small proportion of dolomite, although biogenic forms have nonetheless been described from a series of locations.

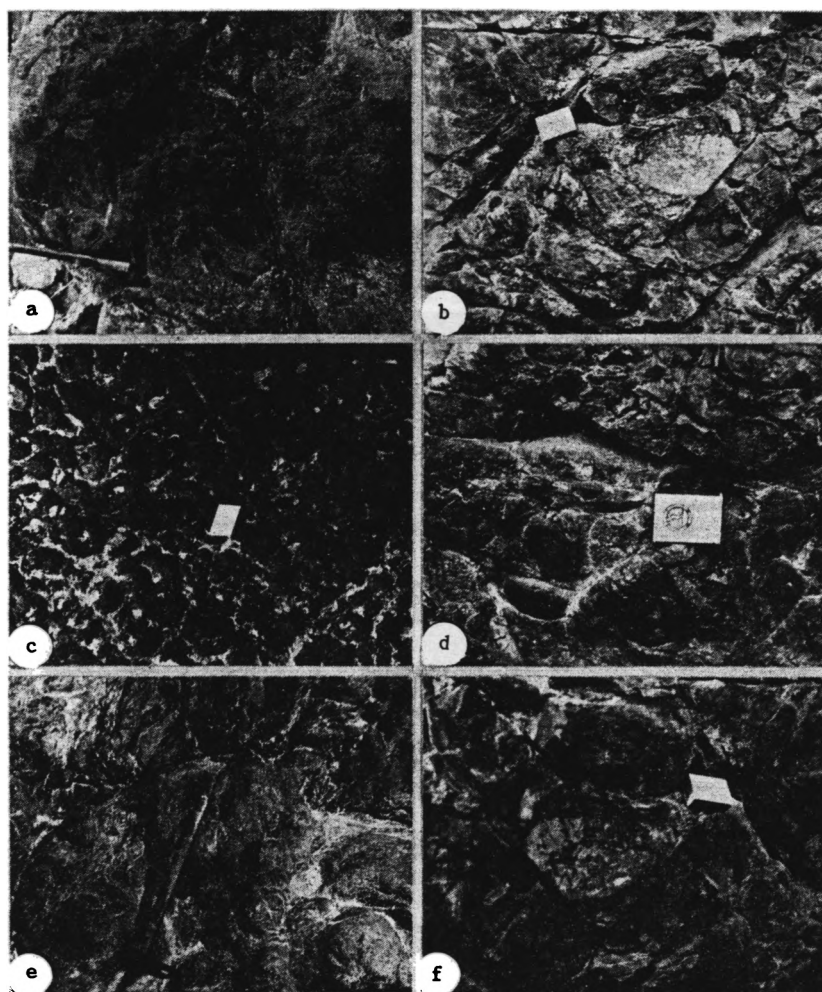


Fig. 2. Nodular and columnar stromatolites. a, b) Nodular stromatolites from the Chichkansky and Chulaktau Suites respectively; c, d) columnar stromatolites in cross section from the Chichkansky and Chulaktau Suites respectively; e, f) large nodular stromatolites from the Chichkansky and Chulaktau Suites respectively.

3. Large rounded-extended nodular stromatolites, up to 70 cm long, stand out from the rocks with sharp relief (Fig. 2e). The same stromatolitic forms may also be observed in the Chulaktau Suite (Fig. 2f). Under the microscope it is clear that both the stromatolites and the intervening rocks are composed of phthanite.

4. Rounded nodular stromatolites occur, 10-20 cm in diameter, and with scattered organic matter (Fig. 3a). The groundmass is composed of crystalline phthanite with volcanic material and small (0.01 mm) quartz grains. Under the microscope, the organic matter appears to have a wavy-banded structure. Similar biogenic structures are quite common in the Chulaktau Suite (Fig. 3b, c). As a rule they are composed of phthanite with rather small phosphatic grains, occasional dispersed chalcedony, and more rare phosphatized spongiolites. They have a carbonate-siliceous groundmass, with black organic matter and fine (0.01 mm) phosphatized quartz grains. The rock is locally brecciated, in which case it is composed of angular to rounded blocks of chert, phosphorite, and shale, with fragments of fine quartz.

5. Plate-shaped biogenic structures are particularly pronounced in the Chichkansky horizon. They are composed of phthanite (Fig. 3d), and are about 120 cm in height. The bases of the "plates" also extend for about 120 cm, and their upper parts become more narrow and rounded, with a hollow interior. They rise above the water in the Chabakty River, and look like baths standing up vertically.

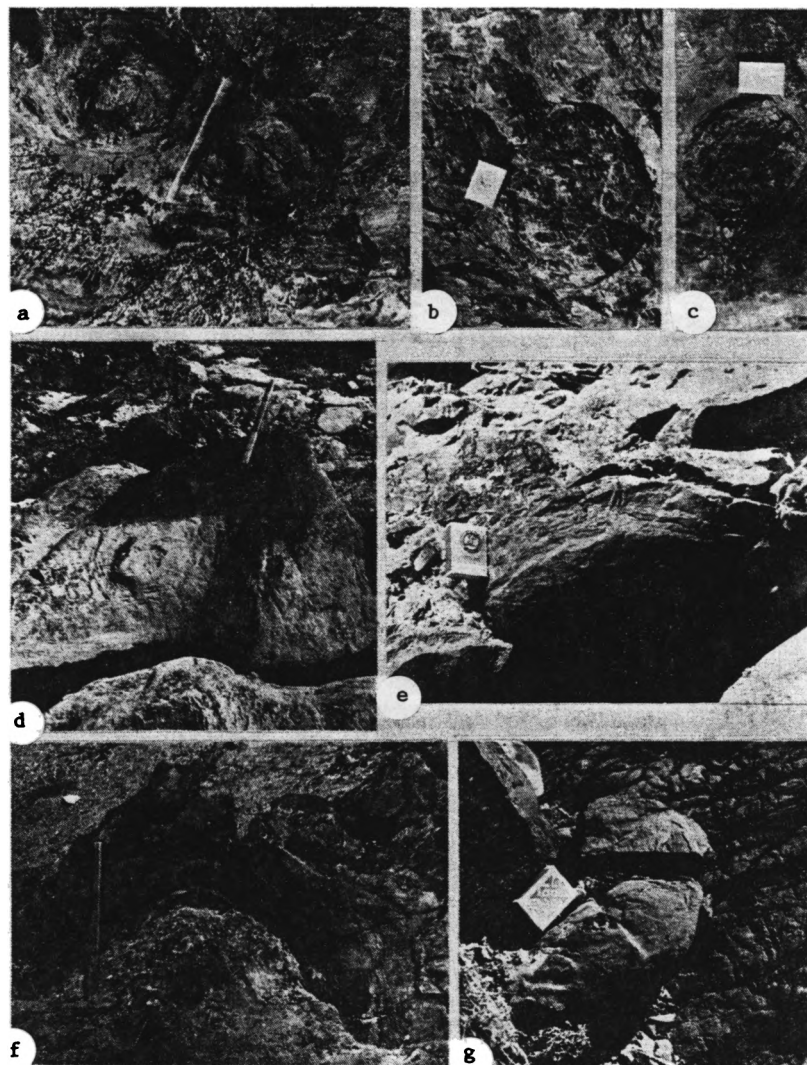


Fig. 3. Nodular stromatolites from the Chichkansu (a, d, f) and Chulaktau (b, c, e, g) Suites.

Despite the fact that these plate-shaped stromatolites draw attention to themselves, many workers [5-8] have neither described nor studied them. Only their existence is mentioned in the literature. This is related to the extreme difficulty in studying these stromatolites. Because of their size, they are impossible to observe in thin section.

6. Plate-like stromatolites occur, which are analogous to the previous type, but far smaller and of a different shape (Fig. 3f). They differ from those described above in that they do not rise to such a height, nor are they as long. Stromatolitic columns with a diameter of around 20 cm sometimes extend around the circumference of the "plates." The inside of the "plate" is frequently infilled by volcanic-carbonate-argillaceous shales, with a greenish hue on account of the content of volcanic material. They are also sometimes surrounded on the outside by the same types of shale.

Plate-shaped stromatolites, but of a far smaller size, are also observed in the Chulaktau Suite (Fig. 3e, g). Bedding is apparent in transverse section, formed from organic matter, or more rarely from phosphorite and phthanite. The thickness of the whole horizon is 11 m.

Alternating Phthanite and Siliceous-Shale Horizon. This horizon begins with a unit of fine, dark-grey, silt-clay shales with a proportion of volcanic material, giving the shales a greenish hue. This bed is 60 cm thick. The shales pass up into siliceous black schistose rocks around 0.5 m thick. Various stromatolitic structures may again be observed in the upper part of this unit: nodules, columns, and rounded inclusions occur, although the schistosity

makes them less clear. They display lamination characteristic of stromatolites. Ten stromatolitic beds can be recognized in this whole unit, which is 12 m thick.

Throughout the Chichkansky Suite, as in the siliceous horizon of the Chulaktau Suite, there is a marked increase in the P_2O_5 content. In the siliceous horizon of the Chulaktau Suite, especially at the top, beds of carbonate-clay shale are observed also. These result from the weathering of phthanite [4]. They also form thin bands.

The analysis of the structure of the Chichkansky and the Chulaktau Suites has shown that the biogenic fabric of the two, in addition to their lithological composition, are very similar. All three types of stromatolitic structure, bedded, nodular, and columnar, occur in both suites.

The formation of stromatolites is a process which depends on a whole range of biochemical and paleogeographical conditions. Maslov [13, 14] related stromatolite formation to shallow-water conditions, since they only live in the light, and he regarded them as restricted to the intertidal zone, with abnormal (variable) salinity (so that they would not usually encounter other marine organisms), characteristic of a lagoonal setting.

This all agrees with the broad conclusions regarding the paleoenvironmental conditions during deposition of the Chulaktau Suite. The evidence includes the widely distributed desiccation cracks, the small thickness of the various horizons in the Chulaktau Suite, its location within the paleobasin, the facies variation in this suite, the presence of conglomerates at the base and the distribution of granule-conglomerates higher up in the suite, and the abundance of oncolites at the top of the productive suite, which are only formed by being rolled continuously on the sea bed by waves. The presence of stromatolitic structures in the Chulaktau Suite is therefore not inconsistent with the lithofacies and the paleogeographic environment during sediment accumulation.

Detailed studies of a series of limestones and newly discovered ore deposits have recently revealed widespread stromatolitic structures within them. They were first encountered in the Belka phosphate deposit at Gornoi Shor'ii in Siberia. Krasil'nikov and Paul' [8, 15] studied them in detail and recognized all three types of stromatolite distinguished at present [9-11]: columnar, nodular and bedded. As shown above, these same three types of stromatolitic structure are also present in the Chichkansky and Chulaktau Suites of Malyi Karatau.

Early Proterozoic stromatolitic phosphorites are recorded from Rajasthan in India [23]. Phosphatic stromatolitic columns in a carbonate cement play an important role. They comprise alternating carbonate-phosphate and siliceous rocks. However, as in the phosphorites of Belka and Malyi Karatau, they are underlain by carbonate stromatolites. Phosphatic stromatolitic columns, cemented by aphanitic phosphorite [20], also occur in the Lesser Himalaya, in Uttar Pradesh (India). Here, on the Pithoragarh River, phosphatized carbonate bioherms are described from the later Precambrian.

Stromatolitic structures are also found in the lower Cambrian phosphatized formations of China [12, 22, 24-26], in the Vendian-Cambrian Kharanursk deposit (Eastern Sayan), in the Precambrian of Nepal [21] and elsewhere.

Further studies of this problem may reveal stromatolitic structures in other phosphate provinces. Why is the relationship between phosphorites and stromatolites so common? Could it be just a coincidence? Was the abundance of blue-green algae conducive to phosphorite formation? Or otherwise, was the abundance of P_2O_5 favorable for the growth of algae? The common connection between phosphorites and stromatolites remains a puzzle for us.

LITERATURE CITED

1. N. G. Brodskaya and V. N. Kholodov, "The possibility of a reefal origin of dolomite in the phosphorite-bearing succession of Malyi Karatau," *Dokl. Akad. Nauk SSSR*, No. 6, 1365-1368 (1965).
2. B. M. Gimmel'farb, Relationship between the Distribution of Phosphorite Deposits in the USSR and their Genetic Classification [in Russian], Nedra, Moscow (1965).
3. B. M. Gimmel'farb, A. M. Tushina, A. N. Smirnov, et al., Composition and Economic Value of Ores from the Main Phosphorite Deposits of the Karatau Basin [in Russian], Nedra, Moscow (1969).
4. T. Dzhumaliev and V. N. Kholodov, "Siliceous rocks from the Chulaktau Suite of Malyi Karatau and their depositional environment," *Dokl. Akad. Nauk SSSR*, 194, No. 2, 414-417 (1970).
5. É. A. Eganov and Yu. K. Sovetov, Karatau: A Model for Phosphorization in the Region [in Russian], Nauka, Novosibirsk (1979).
6. É. A. Eganov, Phosphorization and Stromatolites [in Russian], Nauka, Novosibirsk (1988).
7. B. M. Keller, V. G. Korolev, and I. N. Krylov, "Subdivision of the Upper Proterozoic of Tianshan," *Izd. Akad. Nauk SSSR, Ser. Geol.*, No. 4, 101-105 (1965).

8. N. A. Krasil'nikova and R. K. Paul', Stromatilitic phosphorites of Gornoi Shorii," *Geo. Geofiz.*, No. 1, 63-68 (1983).
9. I. N. Krylov, Riphean and Lower Cambrian Stromatolites of Tianshan and Karatau [in Russian], No. 171, GIN AN SSSR, Moscow (1967).
10. I. N. Krylov, "Riphean and Phanerozoic stromatolites of the USSR," Candidate's Dissertation in Geological and Mineralogical Sciences, GIN AN SSSR, Moscow (1972).
11. I. N. Krylov, Riphean and Phanerozoic Stromatolites of the USSR [in Russian], Nauka, Moscow (1975).
12. É. L'yanzun, "Relationships between the locations of phosphorite deposits in China," Transactions of the 27th International Geological Congress (Section S.15), 1986.
13. V. P. Maslov, "Stromatolites and facies," *Dokl. Akad. Nauk SSSR*, 125, No. 5, 1085-1089 (1959).
14. V. P. Maslov, Stromatolites [in Russian], No. 41, GIN AN SSSR, Moscow (1960).
15. R. K. Paul', "Role of living matter in the formation of phosphorites in Gornoi Shorii and the Irkustsk amphitheater," in: *Role of Biogeochemical Studies in Increasing the Mineral Resources of the USSR* [in Russian], VSEGEI, Leningrad (1986).
16. K. T. Tabyldiev and L. F. Cherbyanova, "Facies conditions in the sedimentary accumulation of phosphorite-bearing successions in the Karatau Basin," in: *The Lithology of Phosphorite-Bearing Deposits* [in Russian], Nauka, Moscow (1976).
17. B. M. Gimmel'farb (ed.), Phosphorites of Karatau [in Russian], GIGKhS, (1969).
18. V. N. Kholodov, Sedimentary Ore Genesis and Metallogenesis in Basins [in Russian], Nauka, Moscow (1973).
19. V. N. Kholodov and A. S. Koryakin, "Origin of phosphatic conglomerate-breccias in Maliy Karatau," *Dokl. Akad. Nauk SSSR*, 135, No. 2, 410-413 (1960).
20. A. D. Ahluwalia, "A synoptic view of the paleontology and petrography of the Tal phosphorite of Mussoorie Garhwal Himalaya, with special reference to microcoprolloid particles," in: *Symposium of 5th International Field Workshop and Seminar on Phosphorite*, 1, Geol. Publ. House, Beijing, 223-225 (1984).
21. R. P. Bashayal, "Stromatolitic phosphorite occurrences in the Lesser Himalaya of far Western Nepal," in: *Phosphorite*, Spec. Publ. Geol. Surv. India, No. 17, 197-206 (1984).
22. Meng Xiaghua, Li Jianhua, Liang Chuanmao, Shan Mansheng, Liu Zhiying, "Analysis of Upper Sinian to Lower Cambrian phosphatic sequences in eastern China and the sedimentation models for phosphorite accumulation," in: *Symposium of 5th International Field Workshop and Seminar on Phosphorite*, 2, Geol. Publ. House, Beijing, 23-51 (1984).
23. Muktinath, V. N. Sant, "Occurrence of algal phosphorite in the Precambrian rocks of Rajasthan," *Current Sci. (India)*, 36, 638 (1967).
24. Zhou Maji, Shen Lhangqi, Zhu Shixing, "Sinian phosphatic stromatolites in South China," *Symposium of 5th International Field Workshop and Seminar on Phosphorite*, 1, Geol. Publ. House, Beijing, 136-137 (1984).
25. Zhu Shixing and Wang Yangeng, "Phosphatic stromatolites in Kaiyang phosphorite deposits, Guizhou, China," in: *Symposium 5th International Field Workshop and Seminar of Phosphorite*, 1 Geol. Publ. Hose, Beijing, 153-164 (1984).
26. Zhu Shixing, Wang Yangeng, Zhang Lin, "Formation of the Kaiyang phosphorites in China as related to ancient microorganisms," *Symposium 5th International Field Workshop and Seminar on Phosphorite*, 1, Geol. Publ. House, Beijing, 181-208 (1984).

FRAGMENTS OF QUARTZ, GRANITOIDS, AND METAMORPHITES IN MIDDLE PALEOZOIC SEDIMENTARY SEQUENCES OF THE SOUTHERN URALS

E. A. Belgorodskii

UDC 552.51:551.75(470.5)

By studying the types of quartz fragments and dated sediments from O_1-O_2 , D_2 and D_3-C_1 , rock fragments of the "straight-through" type are detected for the first time. They are of identical character to quartz inclusions of gneiss-slates from complexes of the Eastern Urals uplift. This confirms the concept that this structure belongs to the residual mountains of the pre-Paleozoic crystalline substrate.

Quartz-containing sandstones are rather widely distributed in the sections of Paleozoic sequences from the eastern slope of the Urals and Western Zaurals. Lithologically, they have been rather poorly and unevenly studied. In these regions there is great value in the dating of the deeply metamorphosed formations which lie in the cores of anticlinal structures — the East Urals and Azurals uplifts, the age of mineralization known in these structures also remains undefined. We earlier obtained the first evidence of erosion of the metamorphites by study of D_2 sediments [3], however the age of the gneiss-slate sequences continues to remain a subject of discussion. One investigator related them to the Carboniferous based on numerous determinations of age by the K-Ar method and attitudes of metamorphic rocks in sections with Vizeisk limestones, others consider them remnants of the pre-Paleozoic crystalline substrate [7], and still others consider them metamorphosed middle Paleozoic eugeosynclinal sediments [9].

An estimate of the prospects for stratiform polymetallic mineralization is an timely and poorly studied problem in the Southern Urals. Numerous appearances of this mineralization are known in D_2 terrigenous-carbonate sequences, but for the majority of these sediments' developmental areas the source of both terrigenous material and of non-ferrous metals is unclear. In recent years, in the Eastern Urals and Zaurals rather numerous zones of copper—molybdenum-porphyrific mineralization are apparent. They are connected with granitoid massifs. In spite of numerous findings of fragments of completely crystalline rocks in dated sediments of the middle Paleozoic, dating of ore bearing porphyric phases continues to remain disputed.

Study of the composition of variously aged clastic sediments, in particular fragments of rocks and quartz with their characteristic indicators, and the establishment of their drift sources, could answer these and a series of other discussed questions. The present article is one of the first attempts to solve these problems on the basis of lithologic investigations. The author has been occupied since the middle 60's with the study of compositional features of middle Devonian sandstones and other detrital rocks from the eastern slopes of the Southern Urals. These investigations got a new impulse connected with leading a geologic survey and by prospecting, in the course of which S. A. Aksenov, V. V. Babkin, A. N. Egorov, and E. P. Shchul'kin were successful in validating the age of many barren sequences by faunal findings, and in establishing their positions in sections in the suture zone between the eastern Urals and Zaurals structures. The efforts of author in these territories were carried out in the frameworks of exploratory and thematic investigations.

Method of Investigation. As was shown by G. G. Lemmlein and V. S. Knyazev, the quartz of terrigenous rocks, as no other mineral, preserves the initial structures which are peculiar to the quartz of the maternal rocks: the color, type of inclusions, character of their distribution, and fracturing [10]. In connection with the limited possibilities for the application of this method to lithified rocks which was proposed by the cited authors, we studied quartz in transparent thin sections in transmitting and reflected light, when the thin section was applied onto black photographic paper. Thin sections of coarse grained sandstones were initially scanned with normal magnifications, and then were described with ocular $\times 10$ and objectives $\times 40-60$. A total of more than 250 thin sections were described, with no fewer than 20-30 grains in each. The character of the distribution and type of inclusions, fracturing, and intergrowths with other minerals

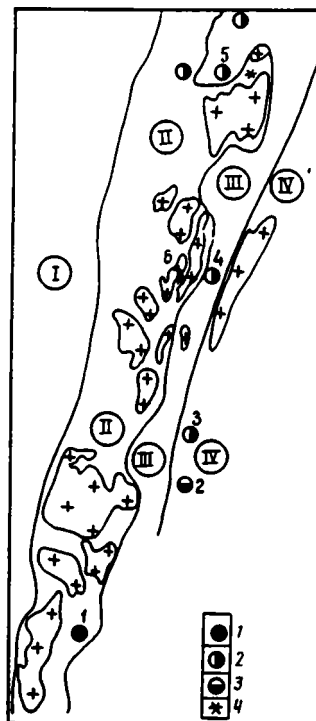


Fig. 1. Distribution scheme for the parts of the lithological investigations. Several granitoid massifs are shown. 1) Ordovician sediments; 2) Middle Devonian sediments; 3) Late Devonian-early Carboniferous sediments; 4) sediments of presumable Ordovician age. Roman numbers: I) Magnitogorsk trough; II) East-Ural uplift; III) East-Ural trough; IV) Zaural uplift. Names of regions: 1) Mt. Maychnaya; 2) Novonikolaevsk occurrence; 3) west margin of Leiptsig pos.; 4) neighborhood of Kosobrosk well; 5) Chelyabinsk region; 6) Kochkarsko-Plastovsk region.

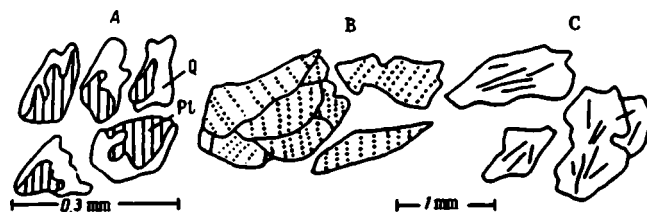


Fig. 2. Several types of fragments from Paleozoic sandstones of the Southern Urals. A) fragments of pegmatoid granites from sandstones of Mayachnaya suite O_1-O_2 ; B)-C) "straight-through" types of fragments: B) fragments of quartz and quartzites with parallel-striated distribution of submicroscopic inclusions; C) the same, with fibroliths.

was recorded in each grain. Thus, in each of the studied sequences, typomorphic associations of minerals and fragments of rock were recognized that did not occur in others. Besides thin sections from the author's collection, thin sections were studied from the collections of S. A. Aksenov, V. V. Babkin, A. N. Egorov, É. P. Shul'kin, E. V. Shalaginov and A. É. Shalaginov. They characterize the dated sequences O_1-O_2 , D_2 , D_3-C_1 , and pre-Paleozoic (?) metamorphites which are breaking through their granitoid intrusions. The distribution of the studied sections is shown in Fig. 1. They all lie in tectonically isolated blocks on the eastern flank of the Eastern Ural uplift and in the suture zone of the Eastern Ural and Zaural structures. The interrelations of Ordovician sediments with younger and older formations have not been established [8]. Middle Devonian sandstones in different blocks with angular and azimuthal unconformities lie on various horizons of Silurian-early Devonian sequences [1, 3], and they locally alternate in sections with basalts and limestones containing fauna of C_1-D_2 . Post-Devonian sediments also unconformably overlap all of the more ancient formations.

TABLE 1. Chemical composition of sandstones of the Mayachnaya suite (1) and its lithologic analogs (5, 6).

Compo- nents	1		6				5				
Al ₂ O ₃	10,92	12,81	14,56	15,3	15,09	11,51	11,8	13,9	16,9	11,5	
Na ₂ O	1,72	1,21	0,53	0,89	4,05	2,23	1,0	2,64	3,97	0,8	
K ₂ O	1,93	1,8	5,24	5,24	2,71	5,24	1,8	2,4	3,58	2,0	
K ₁	1,12	1,5	9,88	5,88	0,66	2,35	1,8	0,9	0,9	2,5	
K ₂	0,10	0,26	0,67	0,39	0,04	0,2	0,15	0,06	0,05	0,2	

Note: K₁ and K₂ are the Middleton coefficients; $K_1 = K_2O/Na_2O$; $K_2 = (Na_2O + K_2O/Al_2O_3)$. All analyses were performed in the laboratory of the Chelyabinsk GRE. The number of the groups of analyses corresponds to the conditional designations in Fig. 1.

Results of Investigations. In studied stratigraphic classifications from Ordovician to Devonian-Carboniferous a characteristic spectrum is established for each sequence of fragments, which together with other signs (features of lamination, color, rock paragenesis, etc.) may be used for the identification of sediments of determined age. Together with these diagnostic indications are reliably recognized "straight-through" types of fragments which are present in all sequences. Quartzite fragments relate to these, including blastopsammitic and sillimanitic (fibrolithic) quartzites and the products of their disintegration. We will discuss several features of these fragments.

In every sequence the fragments of quartz and quartzites possess principally angular fragmental form, indicatings their local origin and short-distance transport. The quartz grains are always identical to the quartz from quartzites; heterogranoblastic and cement milonitic structures with angular boundaries of individual grains predominate in the latter. Quartz with abundant isometric inclusions most often occurs in granoblastic and mylonitized quartzites and the quartz grains from them (Fig. 2). The inclusions are grouped in parallel submicroscopic bands. Such quartz appears noncataclastic in polarized light, but its parallel-cloudy extinction is detected with great magnification. Grains of rose garnet and ore minerals are constantly present among the inclusions, but the largest part of the isometric inclusions is not diagnosed.

The second variety of quartz grains is often connected with fragments of blastopsammitic quartzites. It is distinguished by correlation of isometric inclusions to rough diagonal cleavage (?) fractures. The inclusions are often concentrated in the central part of grains, while the crystal edges are deficient in them. The inclusion distribution is unevenly clustered on the fractures. Along with pink garnet and ore minerals, inclusions of zonal regenerated zircon with rounded, dark-colored, green-brown toned nuclei are rather common, as well as submicroscopic inclusions of crystals with lenticular and drop-like form, similar to xenotime. Fragments of biotite and apatite quartzites and quartz with inclusions of these minerals are common.

Sillimanitic quartzites and the quartz grains from them are distinguished by a minimal quantity of submicroscopic inclusions. the sillimanite (fibrolith) is weakly colored a yellow-green tone, and is diagnosed by high relief, positive elongation, and characteristic crystal habit. The length of sillimanite spicules does not generally exceed 0.02 mm.

The similar mineral composition of the defined inclusions and the weak rounding of the fragments make it possible to confidently connect them with a single source of supply, which is most likely the metamorphic formations of the Eastern Urals uplift. The quartz of the metamorphic rock which developed in this structure is completely identical in its composition and features of inclusion inclusion to the above described fragments.

The composition of sandstones of the Maychnaya suite O₁—O₂ is described in general form by N. F. Mamaev [11] and M. L. Klyuzhin [8]. In our observations, it is made up of fragments of quartzites, porphyries with coarse fused bipyramidal quartz crystals, intergrowths of quartz and plagioclase, and fragments of chalcedonized siltstones. The connecting mass is close in composition to the coarse fragments, and is represented by a quartz-sericite aggregate. The quartz from the porphyries is distinguished by a pink color caused by the inclusion of hematite scales, hematite on biotite, and very scarce hematite and chlorite on olivine (?). Submicroscopic isometric inclusions are often concentrated in the central part of disseminations, and this imparts a zonal structure to it; locally they densely saturate cleavage fractures. The relict remnants of quartz-feldspar rims preserved on several crystals attest to the local character of the material. Fragments of the basic mass of porphyries are common; felsite, recrystallized in an allotriomorphic-granular aggregates. Disseminations of sericitized plagioclase and biotite also occur in fragments of the porphyries. The red-violet color of individual layers in the red-bed sandstones of the Mayachnaya suite is caused by the wide development of fine scales of hematite which densely saturate the cement and rock fragments.

Yet another type of quartz fragments in the described rocks possesses the characteristic form of ichthioglypts (see Fig. 2). It is found in integrowths with sericitized plagioclase, and apparently, belongs to disintegrated pegmatitic granites or pegmatites. These fragments also are unrounded, acutely-angled, and most likely of local occurrence.

Fragments of white and light grey siltstones are made up of sheaflike and spherulitic aggregates of chalcedony. They are grouped in patches and bands of different quantity and form. It looks like they are formed by organic detritus: similar rocks are particularly characteristic for limestones silicified in the zone of hypergenesis. Similar siliceous rocks which are developing in the serpentinite weathering crusts are distinguished by dark color, they are always ferruginized, and they preserve the lattice structure of the initial rocks.

Staurolite, garnet, and zircon are detected in the heavy fraction of sediments of the Mayachnaya suite in synthetic heavy concentrates — from the data of A. É. Shalaginov.

Upper Devonian Sandstones in many regions of the Southern Urals and Zaurals are united by geologists-surveyors into sequences under various local names. As shown in [1], over significant areas their petro-foundation is determined by the erosion of Silurian-early Devonian extrusives, the previous stages of greenschist metamorphism. Predomination of volcanic rock fragments with intermediate and basic composition, feldspar sandstones and siltstones, limestones and variously grained marbles, is characteristic for these clastites. Fragments of quartz and granitoids, diorite porphyrites, serpentinites, and pyroxenites are present. Pyrite-marcasite and siderite concretions are rather widely developed. This determines the high density of the sandstones, which is commensurate with the density of the sandstones, which is commensurate with the density of basalts (2.85-3.1 g/cm³). An admixture of clay kaolinite-hydromica, chlorite, and clay-carbonate material colors the sandstone into grey and green-grey tones. Flysch-type layering and a lower yield (fraction of percent) of the heavy fraction is rather characteristic.

Based on features of the inclusions and the character of fracturing the fragments of quartz and granitoids belong to two types: 1) those with inclusions of zonal zircon and acicular apatite crystals; 2) those with bent rutile twins and short prismatic apatite crystals. Both types of quartz are identical to the quartz of the granitoid massifs of the Kochkarsko-Plastovsk group, which, as was shown above, are related by several investigators to the end of the middle Paleozoic and the late Paleozoic [4, 12].

Layers and packs of quartz sandstones in the D₃-C₁ volcanogenic-sedimentary sequence are distinguished by an abundance of quartz crystals fragments with rounded bipyramidal form similar to the quartz of diorite porphyrites and quartz diorites. In distinction from the quartz of Ordovician sediments, these grains are not fractured, and are colored in light grey tones. Fragments of transparent acid plagioclase and lattice microcline are also noted in the sandstones. Fragments of cataclazed granitoids are common, in which relict hypidiomorphic-granular aggregates are preserved in the form of boudins in a shaley quartz-sericite-chlorite mass. In section of the Novonikolaevsk and Mikheevsk copper-porphyry occurrences quartz sandstones are interlayered with different volcanoclastites of psammitic and psephitic structures. The petro-fund of the latter is determined to a significant degree by the fragments of extrusive and intrusive rocks of the basalt-andesite-dacite (gabbro-diorite-plagiogranodiorite) formation of D₃-C₁. Consideration of the features of these sediments falls outside the limits of the given report, and we will only note the presence of fragments of gabbro, garnet and scapolite skarns, magnetite and pyrite ores, secondary quartzites, limestones, garnet amphibolites, and graphite quartzitic. Fragments of propylitized porphyritic diorites and diorite porphyrites are rather common. These are distinguished from the fragments in the middle Devonian sequences by the basic plagioclase composition, which is replaced by saussurite or carbonate, while fragments in the more ancient sediments contain pure non-cloudy albite.

Discussion of Results. The conducted investigations essentially supplement work completed earlier [1-3, 8, 11]. In our view there is particular value in the establishment of the "straight-through" fragment types which are present in all of the studied sediments. Among these fragments are sillimanite quartzites. Sillimanite, as is known, is a typomorphic mineral of the amphibolite and granulite facies of regional metamorphism [5, 6]. Its formation has not been ascertained in contact aureoles of intrusions. These data make it possible to confirm that even by the early Ordovician, uplifts of metamorphic blocks on the eastern slope of the Southern Urals supplied terrigenous material to the sediments. As far as is known, fragments of amphibolite facies rocks have not been described in Ordovician deposits up to this time. Apparently, the marked similarity between quartz from metamorphic rocks of the Eastern Ural uplift and several granitoid massifs which were evidently formed by anatectic gneiss-amphibolite sequences merits additional and delicate geochemical investigations.

Lithologic and age (?) analogs of the Mayachnaya suite are known in several regions of the Southern Urals. We studied their most northern outcrops in the Chelyabinsk region [2], where they lie at the base of a geosynclinal section; the overlying tuffo-siltstones contain fragments of microcline and alternate with sequences of aphyric basalts. It is named the Dolgoderevenskaya sequence. Fragments of quartz porphyries, pegmatoid plagiogranites, pegmatitic, quartzites, single fragments of amphibolites, and abundant fragments of columnar crystals of biotite replaced by hematite are described in the composition of the sequences's arkosic sediments. This region is 350 km from the

stratotypical section of Mount Mayachnaya, but at both points the sediments represent mature mineral associations which are identical in composition and Middleton coefficient, indicating the significant role of the clay component (Table 1). Sediments of the Dolgoderenskaya sequence display layering characteristic for deposits of intermittent flow and signs of drift of the material from the south: sites presently occupied by the Chelyabinsk granite massif.

Barren arkosic clastites lying on crystalline slates in the Kochkarsko-Plastovsk region (between Chelyabinsk and Mt. Mayachnaya) are similar in every lithological indication to the Ordovician sediments. Coarsely crystalline marbles, silicate-carbonate rocks on marble, and the marmorized Vizeisk limestones are widely represented in sections of this region. Earlier, they were all united into a single sequence with the metamorphites. In recent years, workers have established that deposition of the Vizeisk limestones preceded the numerous deformations of the marbles. It is not excluded that the siliceous siltstones present in fragments in the Mayachnaya suite represent products of pre-Ordovician weathering crusts of these marbles. It is also possible that erosional products of the late Baikalian volcano-intrusive liparite formations are represented in the sediments of the Mayachnaya suite and its lithologic analogs. These formations are known in most complete and representative form in the Polar Urals [4], and the described sediments are similar to it in geochemical specialization (W, Mo, Pb, Zn). The sum of known data make it possible to propose that arkosic sediments of O_1-O_2 were formed by erosion of areal weathering crusts in a subaerial shallow water environment and peneplainized relief, where only stable rocks such as quartzites, fine grained pegmatites, and silicified limestones were preserved on the erosional surface. It is interesting that traces of gold prospecting efforts are preserved in all of the areas where deposits similar to the Mayachnaya suite developed, and in the dumps of workings it is possible to see fragments of nonsulfide quartz veins. Gold's behavior in rocks of various granulometric composition has nowhere been studied. Investigations of these sediments in the indicated direction are represented as extremely promising, not excluding the fact that they may be reservoirs in which the erosion products of ancient gold-bearing mineralization zones were accumulated.

The petro-fund of middle Devonian sandstones in volcanic zones is 60-90% comprised of fragments of extrusives of intermediate and basic composition, and these sediments are practically stripped of quartz clastics [1, 3]. The map abruptly changes with remoteness from the volcanic zones close to the outcrops of gneiss-slate blocks. The quantity of extrusive fragments decreases to a fraction of a percent, and the fragments of granitoids, quartz, and marmorized limestones increase. There are many fragments of siliceous tuffites, tuffo-siltstones, and other siliceous rocks in the psephitic sediments developed among the sandstones. These are rock fragments far from the explosive centers of the zone. Dependences are also observed in the metallogenic specialization of the middle Devonian sediments. In the volcanic zones, where sandstones overlap Silurian-early Devonian association which are accompanied by copper-porphyric and skarn-copper-magnetite mineralization, the sections are saturated by pyrite-marcasite and pyrite concentrations carrying the high contrast geochemical anomalies of chalcophile elements (Zyryankul'-Kul'myakovsk region). Terrigenous and terrigenous-carbonate sequences mapped on the flanks of the gneiss-slate outcrop sequences and the interrupting granitoid massifs with molybdenum and lead-zinc mineralizations, are accompanied by aureoles of these elements (Yvel'sk zone).

Many years of geologic prospecting efforts in the areas of D_2 sedimentary sequence development, where an array of prospecting indications of pyrite-polymetallic mineralization is known, have not led to the discovery of any significant ore accumulations. Meanwhile, the Amursk pyrite-polymetallic occurrence is known in the quartz-siltstone-carbonate D_2 sequences on the western limb of the Eastern Urals uplift; the ore containing deposits represent an association having no facies analog in other zones and no lateral transitions to polymict or quartz sandstones sequences predominating in D_2 .

In our opinion, sections of D_2 in the Western Zaurals are the largest prospects for discovery of the stratiform type of ores. They, in distinction from those considered above, are distinguished by wide development of finely detrital facies, red and mottled color, high background contents of chalcophyllite elements, and contamination by sulfides over vast areas. Drift of detrital material from the west is established by a single observation of sloping layering and orientation of beach pebbles. This drift is from Eastern Ural zones, which apparently served as a source of terrigenous components and of colored metals. It is possible to suppose that here, as in the region of the Amursk occurrence, chemical-biogenic thickening of sulfides was not overwhelmed by the introduction of a great volume of clastics, and that it occurred in an environment of sluggish sedimentation. Late Devonian deposits in the Zaurals are poorly studied up to the present time. Geological observations in this zone are hindered by poor exposure and the development of a cover of Meso-Cenozoic sediments.

The wide distribution of granitoid fragments in the petro-fund of Devonian and Carboniferous sediments, their characteristic features, and the poor working of clastic material make it possible to connect these fragments with the denudation of actual massifs in the Eastern Urals uplift. However, many of them have intrusive contacts with middle Paleozoic formations, contain their xenoliths, and are surrounded by contrasting contact aureoles. Apparently, intrusions of varied formations belonging to variously aged stages of the tectonomagmatic history of the Uralides are spatially

combined in the limits of large massifs (Plasovsk, Chelyabinsk, etc.). Middle Paleozoic granitoids in large part occur on the marginal parts of the uplift, and in the course of geosyncline development they undergo numerous reworkings and activation. One form of the latter may be contrast block uplifts which evolve out of massifs on the eroded surface. Further study of granitoid fragments in clastic sediments, with the help of delicate geochemical methods and comparison with actual massifs, makes it possible to substantially refine the age of the intrusions, which had earlier been united in a single intrusive complex. Many of the massifs in the structure of the Eastern Urals uplift and the volcanic zones surrounding it are regionally altered by processes of propylitization. It is possible to suppose that in the Urals, as in other porphyry-copper provinces of the USSR and the world, ore bearing phases developed repeatedly and polycyclically.

It is possible to conclude:

1. The predomination of detrital material of local occurrence in the studied sediments, its poor working, and the presence of "straight-through" type fragments (the erosional products of formations of amphibolite facies) confirm the concept that blocks of metamorphic rocks belong to remnants of the Precambrian crystalline substrate. In the Paleozoic this substrate was repeatedly activated under the influence of eugeosynclinal processes and variously aged granitoid magmatism is developed within its limits.

2. The appearance of indications of pre-early Ordovician hypergene crust formation makes it possible to question the possible detection of ancient precious metal placers which were redeposited by intermittent flows from root sources in deposits of O_1-O_2 . The rather wide distribution of sediments basically identical to the lithologic indications of the stratotype of the Mayachnaya suite gives this problem special timeliness.

3. To a significant degree, the studied terrigenous sediments inherit the geochemical specifics of the maternal rocks of the supply region. It is possible to suppose that the majority of areas of middle Devonian sediment development in the Eastern Urals zones, where psammitic clastites predominate, have low promise for the detection of stratiform mineralization of colored metals. The Zaurals zones, which are removed from the active accumulation basins of terrigenous components, have great promise in this mineralization even by climatic factor.

LITERATURE CITED

1. E. A. Belgorodskii, "Middle Devonian volcano-mictite sandstones of the Kunashaks region. Paleo-vulcanism of the Urals," Tr. IGG UNTs AN SSSR, No. 113, 185-192 (1975).
2. E. A. Belgorodskii and É. V. Shalaginov, "On volcanoclastic rocks of acid composition in the northern setting of the Chelyabinsk granite massif," in: Petrography of Detrital Rocks of the Eastern Slope of the Urals and Mugodzhars [in Russian], IGG UNTs AN SSSR, Sverdlovsk (1976), pp. 22-26.
3. E. A. Belgorodskii, Volcanogenic Formations and Facies of the Alapaevsko-Chelyabinsk Zone, an Example of the Kunashaksk Region, Dis. Kand. Geol.-Min. Nauk., IFF UNTs AN SSSR, Sverdlovsk (1979).
4. Geology of the USSR [in Russian], Vol. 12, Part 1, Nedra, Moscow (1973).
5. W. A. Deer, R. A. Howie, and J. Zussman, Rock-Forming Minerals [Russian translation], Vol. 1, Mir, Moscow (1965).
6. N. L. Dobretsov, V. S. Sobolev, and V. S. Khlestov, Facies of Regional Metamorphism of Moderate Pressures [in Russian], Nedra, Moscow (1972).
7. K. K. Zoloev, M. S. Rapoport, B. A. Popov, et al., Geologic Development and Metallogenesis of the Urals [in Russian], Nedra, Moscow (1981).
8. M. L. Klyuzhina, Paleogeography of the Urals in the Ordovician Period [in Russian], Nauka, Moscow (1985).
9. V. A. Koroteev, T. V. Dianova, and L. Ya. Kabanova (1979), Middle Paleozoic Vulcanism of the Eastern Zone of the Urals [in Russian], Nauka, Moscow (1979).
10. G. G. Lemlein and V. S. Knyazev, "Test study of detrital quartz," Izv. AN SSSR, Ser. Geol., No. 4, 94-96 (1951).
11. N. F. Mamaev, "Geologic structure and history of development of the eastern slope of the Southern Urals," Tr. IGG UF AN SSSR, No. 73 (1965).
12. G. B. Fershtater and N. S. Borodina, Petrology of Magmatic Granitoids (an Example from the Urals) [in Russian], Nauka, Moscow (1975).

LITHOLOGIC CRITERIA FOR PREDICTION OF AUTHIGENIC SULFUR DEPOSITS IN HALOGENOUS FORMATIONS

V. F. Polkunov

UDC 553.66:553.63

Lithologic criteria for prediction of sulfur prospects of halogenous formations are discussed. Epigenetic gypsum-containing formations are shown to be the source and localization area of sulfur placers; they also determine the structural-geological position of these placers as specific products of gypsum weathering.

Important contributions to the study of the patterns of localization, distribution, and prediction criteria of sulfur mineralization in halogenous formations have been made by Uklonskii, Korotov, Sokolov, Yushkin, Pisarchik, Belenitskaya, Korenevskii, and others. The reliability of criteria based on the concept of metasomatic placer formation has been borne out by discoveries of new ore bodies.

During the last decade, Kropacheva proposed a group of lithologic predictive criteria (see [9, 10] and other publications) to supplement existing ones. She asserted that mineralization is controlled by lithologic facies and that this process is expressed in the localization of sulfur placers amid littoral shallow-water and mixed-composition carbonate-sulfate rocks. A lithologic-facies criterion for prediction of deposits was proposed on this basis. According to Kropacheva, for example, in the Ciscarpathian region the lithologic facies of sulfate strata with porphyroid structures containing an average of 20-50% of sedimentary carbonates are most favorable for sulfur mineralization. According to this theory the source of selectivity of "sulfur metasomatism" and higher permeability of rocks is residues in their structures. Kropacheva recommended prospecting for deposits in areas with widespread carbonate-sulfate rocks that developed (or possessed during sedimentation) layered or porphyroid structures. The presence of such structures is claimed to be the mandatory requirement for the deposits to have evolved; a lithologic-structural criterion of commercial sulfur availability was proposed. According to Kropacheva, most sulfate deposits are situated on areas where thick organogenic carbonate rock beds are found at the base of parent formations. She concluded that deposits tend to be associated with syndimentary elevations in marginal parts of paleobasins founded before evaporites accumulated. In her view, this leads to a local predictive criterion. She concluded that sulfate-bearing formations belong to section types I and II after Krumbein [15] and that the medium- and small-scale prognoses should rely on this formational criterion.

In the present paper we discuss the lithologic criteria for the commercial sulfur prospects of halogenous formations suggested by Kropacheva in light of available relevant data.

In his studies of the Ciscarpathian region (one of the oldest sulfur mining regions in Europe), Pusch [20] concluded 150 years ago that gypsum is the only possible source of exogenous sulfur. Even earlier, Oczko [16] wrote of the spatial correlation between oil and sulfur deposits. The chemical composition of primary rocks has the main role in formation of sulfur ores, because calcite and authigenic sulfur can only be formed as a result of interaction of sulfate-ions with ore-forming agents. Kropacheva agrees with that view. All nonsulfate components of carbonate-sulfate complexes are passively transferred to the ore without participating in the chemistry of metasomatism.

The sulfur content in (mineral) gypsum is 18.63%. With a content of 20-50% of sedimentary carbonates we can calculate that mixed-composition rocks can form only poor (10-18% S) or unprotective ores with a sulfur component of less than 10%. On the other hand, in ores formed after rocks of a homogeneous sulfate composition, sulfur is usually contained in amounts higher than the theoretical concentration of gypsums. Its concentration in anticlines (decompression zones) is attributed to the hydraulically determined influx of sulfide ions created with SO_4 is reduced in parent rocks from adjacent synclines (compression zones). At locations of SO_4 reduction and migration, metasomatic limestones with noncommercial quantities of sulfur or with no sulfur are left. Sulfur concentration varies in secondary-unaltered limestone ores that make up 90% of placers and contain 98% of proven sulfur reserves; in the Soviet Ciscarpathians, it has a range of 5-15%. The uniform content of the sulfur component in this ore type indicates that ore bodies were

Institute of Geology and Geochemistry of Fossil Fuels, Academy of Sciences of the Ukrainian SSR, Lvov. Translated from *Litologiya i Poleznye Iskopaemye*, No. 2, pp. 105-114, March-April, 1990. Original article submitted October 10, 1986.

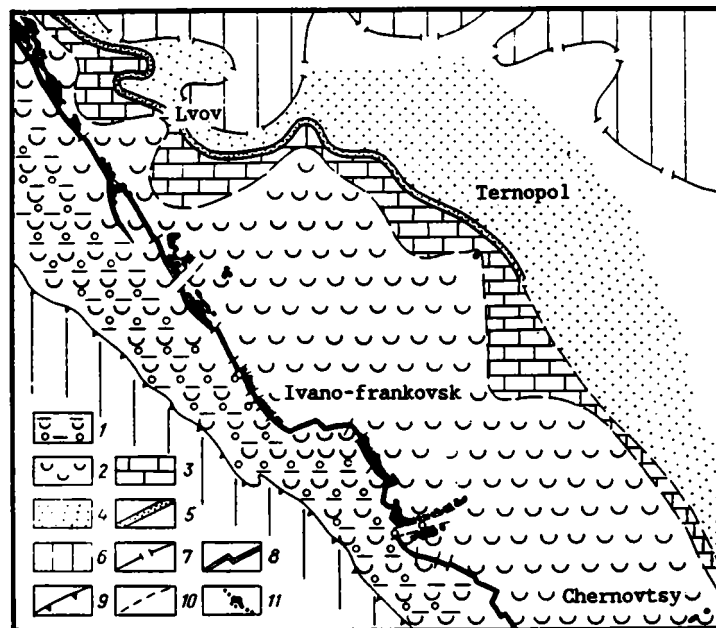


Fig. 1. Distribution of sulfur placers and lithofacies complexes of Tirassy halogenous formation in the Soviet Ciscaucasian region (reconstruction), compiled with the use of data from Kudrin [11]. Lithofacies complexes: 1) clay-salt-gypsum; 2) gypsum; 3) limestone; 4) sand; 5) clay-sand facies of bay barrier; 6) areas with no Badenian sediments; 7) recent boundaries of Badenian sediments; 8) tectonic zone of conjugation of East European Platform with the Ciscaucasian foredeep; 9) coastal Carpathian overthrust; 10) other faults; 11) authigenic sulfur placers.

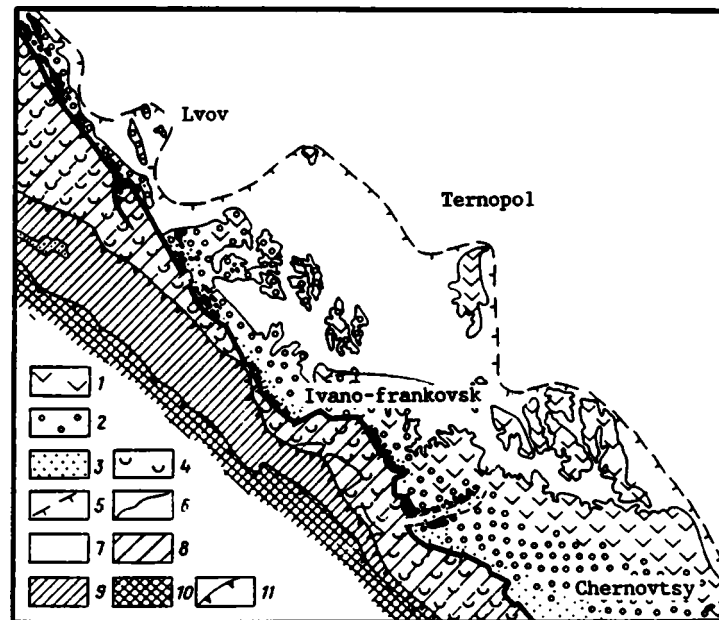


Fig. 2. Secondary zoning of the sulfate complex of the Tirassy Formation and distribution of sulfur mineralization in the Soviet Ciscaucasian region: 1-4) occurrence zones 1 — sedimentary gypsum, 2 — epigenetic gypsum, 3 — gypsum anhydrite, 4 — rock salt, clay, postsedimentary anhydrite); 5-6) sulfate complex boundaries (5 — hypothetical original, 6 — recent); 7) Volyn-Podolye margin of the East European Platform; 8-9) Ciscaucasian foredeep (8 — external zone, 9 — internal zone); 10) Carpathians; 11) Stebnik overthrust. Other notations as in Fig. 1.

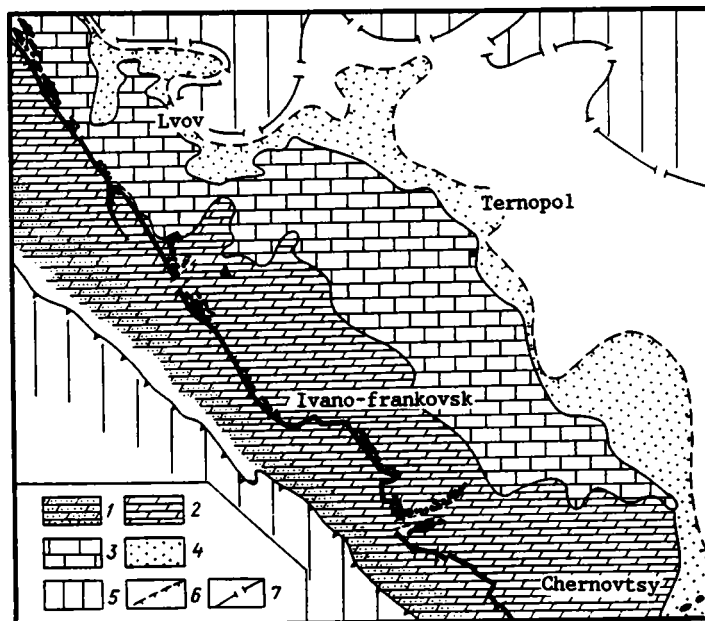


Fig. 3. Distribution of sulfur placers and lithofacies complexes of the Early Badenian in the Soviet Ciscarpathian region (reconstruction) compiled with the use of materials from Kudrin [11]: 1-4) lithofacies complex (1 — sand); 5) areas with no Badenian sediments; 6-7) recent boundaries of Badenian sediments (6 — Early, 7 — Late). Other notations as in Figs. 1 and 2.

formed here from lithologically homogeneous gypsum rocks. More than half of the ore in the Soviet Ciscarpathian region and the Tarnobrzeg ore field in Poland are of the rich category. Only poor ores which uneven sulfur concentrations are formed after mixed rocks. This is observed, for example, in deposits of the middle Volga region and Dagestan. They were formed after sulfate-carbonate-clay sediments. The mixed composition of parent rocks is a negative factor in origination of rich and stable mineralization.

The association of ore accumulation with peripheral carbonate-sulfate complexes of halogenous formations is explained by the fact that in marginal parts of evaporitic basins more carbonates — and later calcium sulfates — were deposited than in deeper portions, where halitic sections prevail [5]. That does not rule out the occurrence of sulfate sediments in central parts of recent evaporitic areas. Deposits of the middle Volga region are situated almost at the center of the Late Permian paleobasin rather than at its margin. In Iraq, ore bodies are also found close to the center of the area occupied by the halogenous formation of the Lower Fars (Middle Miocene).

The main sulfur formation of the Ciscarpathian region is the middle miocene-upper Badenian Tirassy Formation. In the northwest the littoral part of the Tirassy basin covers the edge of the West European Platform. However, large sulfur concentrations are established here only in the Tarnobrzeg ore field, situated at the juncture of the West European and East European Platforms and the Ciscarpathian foredeep. On the remaining area of the tidal zone of the basin, where sebkha facies may have existed, are the Czarkowy, Posadzy, Swoszowince and other placers, with ores that are the poorest in that region. In the Soviet Ciscarpathian area, the narrow zone of commercial sulfur mineralization stretches along the diagonal of the paleobasin; it is associated with the juncture of the platform and the foredeep. Regional faults which bound these structures cross sediments of all possible facies. However, there are no commercial placers in littoral facies sediments. These sediments consist of sand, clay-sand, and calcareous units [11]. Ore bodies are situated regularly along the tectonic juncture of the platform margin with the foredeep, 10-60 km from the sediments of the littoral facies, mainly at the center of the area occupied by halogenous deposits (Fig. 1). Other examples can be cited to the effect that littoral facies and facies complexes of paleosebkha do not play a major role in sulfur mineralization and do not determine the position of sulfur deposits among evaporites. Sediments of recent sebkhas on the shores of the Persian Gulf, the southern Mediterranean, the Red Sea, and other bodies of water characteristically contain more nonsulfate than sulfate components.

Metasomatoses in "favorable" rocks, especially gypsum rocks with formation of sulfur ores, are controlled by structural tectonic factors. Permeability in geologic bodies develops as a result of deformation by tectonic motions, as

described in well-known studies by Kreiter, Smirnov, Vol'fson, Yakovlev, Korolev, and Shekhtman. Metasomatic sulfur placers were also formed in tectonic stress fields with deformation of anisotropic parent rock bodies. However, the specifics of the gypsum-anhydrite-gypsum system were most important in the development of permeability to ore-forming agents.

Petrographic studies show that tectonic disruptions of parent rocks — fissuring, layer, etc. — are insufficient for ore development. A massive destruction of the very crystals of sulfate minerals is necessary for this process. It occurs by gypsification of anhydrites during inversion of motions.

Tirassy gypsums of the Ciscarpathian region, that subsided to a great depth at the end of the Badenian, were dehydrated and transformed to anhydrites. Since the Early Postsarmatian, anhydrites have been (and still are) continually brought to subsurface environments. By hydration they are converted via gypsum anhydrites to secondary gypsums — the crust of weathering of anhydrites. The zonal distribution of postsedimentary neomorphs in the region presents a continuous series of evolutionary transformations of an unstable mineralogic system: sedimentary gypsum → anhydrite → gypsum anhydrite → epigenetic gypsum → sulfur placers. The latter appear as a locally developed crust of weathering of epigenetic gypsum. On the Volyn-Podolye platform margin, at least 95% of proven sulfur accumulations are in the zone of epigenetic gypsum anhydrites and gypsums (Fig. 2). On Ciscarpathian deposits, the gypsification of anhydrite has been found to precede development of fine initial calcite and sulfur segregates [1]. They are only found in areas of microcracked crystals that later were converted to gypsum by hydration. Thus, calcite and sulfur substitute massively epigenetic gypsum as such rather than sulfate minerals in general, contrary to what is often claimed. Gypsification and formation of sulfur-calcite pseudomorphoses after gypsum crystals are consistently correlated. As anhydrite crystals are converted to gypsum, they take in water, grow in volume, and become cracked and fractured. The volume increase can be as large as 67% [7]. When occurring at a shallow depth, anhydritic bodies subjected to gypsification swell and grow in thickness. Low-angle bulging elevations appear in the relief, and the layers become plicated and "wavy." A dense network of cracks and brecciation appear. The deformation affects also the enclosing rocks. A fine disharmonic folding and brecciation of hard layers can be observed in the walls of overburden ledges of Ciscarpathian sulfur quarries in clays and marls of placer roofs. The positive pressure that arises inside anhydrite bodies during gypsification can be as high as 20–600 kg/cm² at depths of 30–150 m. Relaxation of this pressure produces peculiar explosions that form the rubble of crystallizational gypsum breccia [2]. In the Ciscarpathian region, over 30% of ores exhibit a breccialike structure. Ores with this structure and gypsum and gypsum-marl breccias are also common in Sicily and Iraq [17, 18]. Secondary gypsum anhydrites and gypsum are replaced by sulfur ores in the Gaurdak ore field in Turkmenia, in the middle Volga region, Daghestan, etc.

The ultimate strength of anhydrite is several times that of gypsum. Ruptures creating ducts for ore-forming agents are not as easily formed in mineral anhydrite and rock as in gypsum. Therefore, anhydritic rock is less permeable in the bed and less favorable than gypsum rock for large-scale mineralization. According to published data, there are no commercial deposits in the anhydritic strata of Eurasia.

The intensity of gypsification depends on rock occurrence depth and fissuring. In almost all halogenous formations filling depressions, epigenetic gypsoanhydrites and gypsum and occupy elevated margins on the day surface or near it. Usually, they are predominant in the most zones at junctures of tectonic blocks. The marginal parts of troughs and depressions experience the most stress during ascending and descending motions. Relaxation of these stresses produces a dense network of faults. Gypsums and related deposits are located not only on elevated sides of troughs and depressions; they are also found inside depressions, but always within those blocks where anhydrites had been brought to weathering levels by vertical motion. For example, in all sulfur placers in Sicily are localized the Sicilian trough. Anhydrites are preserved on less mobile portions of the island or subsided parts of depressions.

The depth of occurrence of primary and secondary gypsum in large and thick geologic bodies depends on several factors, mostly it does not exceed 500 m [3]. Over 90% of the world's exogenous sulfur reserves is found at depths of less than 500 m. Deeper sulfate formations contain only dissemination haloes of sulfur or extremely rare morphologically unstable ore accumulations with poor technological characteristics, primarily poor permeability to the heater carrier used in underground sulfur melting (USM). The literature mentions just one case of mining of ores in caprock on the side of the salt dome in the Gulf of Mexico at a depth of some 800 m [2]. Attempts at mining placers at depths of over 1000 m by USM undertaken in the Canada in the early 1960s proved a failure [21]. There is no other information on attempts at sulfur extraction from continuous sulfate or carbonate-sulfate strata at such depths. A depth of up to 500 m appears to be the limit for cost-effective exploration.

Anhydrite gypsification and the gypsum tectonics related to it are the elements of the ore formation process that "loosen" diversely structured parent rocks. These elements, rather than interlayers of sedimentary carbonate rocks and structures, are responsible for the high permeability and conductivity of ore-forming agents in rocks and crystals. It is an important peculiarity of sulfur mineralization. During the course of evolution and repeated modification of crystals, structures and textures of sedimentary gypsum are converted to secondary structures and textures of anhydrites and

gypsoanhydrites, and then epigenetic gypsum, including secondary plicated and porphyroid structures of these rocks. With their substantively new ore structures, sulfur ores finally inherit just relicts of the relicts of the original sedimentary rock structures. These are preserved in ores mainly in the striation that is common and reflects rhythmic alternation of thin layers with different quantities of nonsulfate components. Ores with stratiform structures are common in the Ciscarpathian region, Turkmenia, Iraq, Sicily, etc. However, all rocks of halogenous and other sedimentary formations were stratified originally.

Krumbein identifies four types of sections, characterizing the stratigraphic position of halogenous formations among enclosing rocks. Type I includes sections where the formations are enclosed in marine sediments. Type II are the sections underlain by marine sediments but covered by red rocks. The most common (quantitatively and regionally) and the thickest formations are found in sections of types I and II. On large areas where they are found, deposits with considerable total amounts of sulfur are located. Sections types III and IV are distinguished by the fact that formations are underlain by red rocks; in type IV they are also overlain by them. In type III, marine sediments are found in the formation roof. These section types typically contain thin and less common formations of mainly marginal parts of folded regions — intermontane depressions and external and internal synclinal structures [4]. The limited occurrence and sulfur accumulations and the relatively small areas occupied by thin parent rocks, often with a noticeable content of nonsulfate components, are easily understandable.

Halogenous formations underlain by thick carbonate strata are mainly chloridic or partially sulfate-chloridic [6]. Ivanov and Levitskii [4] emphasize that carbonate rocks are predominant in the marine complex of sediments enclosing halogenous formations. Obviously, some of these deposits occur on precisely such rocks; however, this is not necessary. In the Soviet Ciscarpathian region, placers cluster less near the bed of bioherm limestones than regularly in a 5-6 km belt adjacent to the tectonic juncture of a platformal margin with the trough (Fig. 3). There are no signs of bed erosion in the southeastern part of the region. In the Polish Ciscarpathian region, small areas of gypsum and gypsum-anhydrite at the Tarnobrzeg ore field lie on thin organogenic limestone [19]. At the foot of the formation at Messina (Sicily), "basal limestone" occurs in the principal Enna-Caltanissetta sulfur mining province. These limestones are evaporitic and not organogenic. However, even these limestones are absent in some of the deposits on the island [17]. At the base of the enclosing formations of many of the sulfur placers on the globe, there are neither organogenic nor evaporitic carbonate rocks.

Extensive and thick (mainly Cambrian, Devonian, and Permian) formations are widespread in Eurasia [5]. However, they contain less than 5% of the continent's proven sulfur reserves. Mesozoic and pre-Miocene Cenozoic formations account for just 5-7% of sulfur concentrations. Commercial placers are rare and usually small in all pre-Neogene formations. In thick sulfate complexes of Miocene formations (Tirassy, Lower Farse, and Messinian) and total of 90% of the exogenous sulfur accumulations on the entire continent is concentrated.

The scale of mineralization depends not only on the size and age of the formation. Thus, the Tirassy formation in the Ciscarpathian region and the Paleogene formation in Fergana lie in the same section type (I). However, they belong to different structural-facies formation types. The former is a foredeep formation, the latter an internal intermontane depression [4]. Likewise, the Upper Jurassic Gaurdak-Kugitanga formations belongs to the structural-facies type of synclises and depressions; the Lower Permian formation of the uplands and bars of platforms in the middle Volga region and the Lower Farse foredeep formations in Iraq are enclosing sections of type II. The structural-facies types of formations are quite different in size of mineralization components. Sulfur concentrations in the Tirassy and Lower Farse formations are higher than the sulfur content of all other formations of the world in section types I-IV. The structural-facies type of any halogenous formation rather than the type of enclosing section is obviously the controlling factor of its potential sulfur prospects.

A concentration of ores on only those areas that have experienced recent elevations is a process that still continues is typical for all sulfur-bearing formations. This fact was noted long ago by Yushkin. Commercially important sulfur formations in Europe (Tirassy and Messinian) are situated in mobile regions adjacent to recent boundaries of the collision of the Eurasian and African Plates. The boundary lies across the Alps, the Apennines, the Carpathians, the Crimea, the Caucasus, the Kopetdag, etc. [14]. Deposits in the halogenous formations of Daghestan and Central Asia are also located close to this boundary. The sediments of the principal sulfur formation of Asia (the Lower Farse) are situated at the boundary between the Arabian and Eurasian Plates. The Tirassy, Messinian, and Lower Farse formations are in the development region of the youngest continental crust, formed at the very end of the Miocene. In the Alpine-Himalayan seismotectonic folded belt and the adjacent platform margins, they occur in zones of new and recent activation. Inside the belt and on neighboring territories that together make the Mediterranean sulfur province, commercially significant deposits are found in those areas of sulfate-containing sediments where blocks of different mobility come in contact.

The distribution of deposits is controlled by faults that cut across evaporites of various facies. Deposits are arranged linearly along the block-bounding faults. Placers cluster in tectonic nodes — at intersections or branchings of

faults — and are localized in anticlinal elements of near-fault folds. The latter has nothing to do with synsedimentary elevations. In all sulfur ore regions of Eurasian, the ore-locating structures arose during the Pliocene; they are so young that sometimes they are expressed in the relief features (in Ciscarpathian region, middle Volga region, Sicily, Iraq, etc.) The neotectonics of these regions have been described elsewhere. For metasomatic sulfur deposits, linear-nodal and zonal distributions are typical, rather than the location in basins, as is characteristic of sedimentary minerals. This can be illustrated by the Ciscarpathian sulfur one belt (see Figs. 1-3). The position of sulfur ore belts (structural-formational zones and deposits) is controlled neither by facies and structural features of parent rocks, nor by the presence of underlying organogenic carbonate rocks, nor by the type of surrounding sections, but by the position of sulfate complexes, the new and recent structures formed much later than the deposition time of the halogenous formations.

* * *

The following three main conclusions can be drawn from the preceding discussion.

1. The "lithologic-facies" criterion directs predictive investigations and prospecting efforts toward finding poor or even noncommercial ores. A revision of Sokolov's conclusions [13] and other theories assigning the development of major placers of high-grade ores to thick bodies of solid surface ores is unsubstantiated. The "lithologic-textural" criterion cannot be a distinctive feature of commercial sulfur deposits. The "formational" criterion direct prospecting efforts at medium- and small-scale precitive exploration of mostly ore-free anhydrites on more than 80% of areas occupied by halogenous formations in the USSR. Assuming that deposits tend to be located on elevations founded before the beginning of the accumulation of evaporites, we would have to acknowledge that the elevations associated with deposits and expressed in modern topography as watersheds of local hydraulic networks measuring a few square kilometers in area — such as locations of deposits in the middle Volga region — have existed since before the Late Permian. This is obviously a far-fetched criterion for "local" prognoses. The predictive criteria proposed by Kropacheva convey no consistent and stable features of commercial sulfur prospects of halogenous formations.

2. The epigenetic gypsum prospects of sulfate-containing lithofacies complexes is a consistent and statistically stable characteristic of potential ore presence. It has been established in all the sulfur-mining provinces of Eurasia. Gypsification and gypsum tectonics are independent of structural features of the paleogeography of the sedimentation of sulfate and carbonate-sulfate rocks or the position of halogenous formations in surrounding strata. The fields and depth of gypsum-containing entities — the source and container of the sulfur ore matter — determine their specific structural-geologic position as deposits of weathering on evaporate occurrence territories. They limit and specify both the area and the depth for predictions and commercial prospecting. This familiar feature should be utilized as a criterion for medium- and large-scale prognoses. It strengthens the primary lithologic criteria of forecasting the sulfur prospects of all halogenous formations — their general abundance in sulfates [12], which justifies predictive studies on any scale. A major objective in lithologic-facies analysis of formations by forecasters is to establish gypsum-containing rocks with highest gypsum concentrations that are favorable to sulfur ore formation. This is a major factor controlling high sulfur content in ores: it is a good technical and economic indicator of the commercial quality of ores. On their basis, one could reduce exploration area and costs by avoiding exploration of poor or noncommercial deposits. This would make it possible to pinpoint locations with the most likely concentrations of mainly rich or medium-grade ores.

3. Gypsum as a criterion of ore prospects is found on extensive areas and in thick geologic bodies of sulfate-containing sediments in mobile zones of new and recent elevations in seismotectonic region of the youngest continental crust and adjacent territories near active boundaries of lithospheric plates within oil and gas provinces and basins.

Additional efforts will be needed to continue work on formulating a set of lithologic criteria. On the other hand, better substantiation of forecasts calls for proper generalization and objective analysis of available data on sulfur in halogenous formations and a synthesis of these observations in a theory of mineralization of exogenous authigenic sulfur. A scientific basis should be built for specifying optimal detailed predictive-exploratory sets of features [8] of the various potential sulfur-bearing provinces in the USSR.

LITERATURE CITED

1. L. D. Arkhipova, A. I. Kostrovskaya, V. F. Polkunov, and Ya. T. Roskosh, "Sulfur mineralization in sulfate rocks," in: *Structure and Distribution Patterns of Sulfur Deposits in the USSR* [in Russian], Naukova Dumka, Kiev, pp. 143-152, (1979).
2. R. Bates, *Geology of Nonmetallic Minerals* [Russian translation], Mir, Moscow (1965).
3. K. A. Gorbunova, "Hydration of anhydrite and concomitant processes," *Tr. In-ta Geol. Geokhim. UNTs, Akad. Nauk SSSR*, No. 140, 35-41 (1979).

4. A. A. Ivanov and Yu. F. Levitskii, *Geology of Halogenous Sediments (Formations) in the USSR* [in Russian], Gosgeoltekhizdat, Moscow (1960).
5. Yu. A. Ivanov, "Salt basins of Eurasia," in: *Geological Structure and Oil and Gas Prospects of Salt Dome Basins of Continents Based on Geophysical Data* [in Russian], Nedra, Moscow, pp. 7-16 (1977).
6. S. M. Korenevskii, *Set of Minerals of Halogenous Formations* [in Russian], Nedra, Moscow (1973).
7. Yu. A. Kosygin, *Tectonics* [in Russian], Nedra, Moscow (1969).
8. A. I. Krivtsov and V. A. Narseev, "Geologic prospecting and predictive-exploratory complexes," *Sov. Geol.*, No. 1, 17-27 (1983).
9. S. K. Kropacheva, "Lithologic-facies of sulfate rocks and their effect on sulfur formation," in: *Lithology, Mineralogy, and Geochemistry of Authigenic Sulfur Deposits* [in Russian], Naukova Dumka, Kiev, pp. 53-69 (1980).
10. S. K. Kropacheva, *Comparative Investigation of the Structure Sulfur-Bearing Halogenous Formations* [in Russian], Nedra, Moscow (1981).
11. L. N. Kudrin, *Stratigraphy, Facies, and Ecological Analysis of the Fauna of Paleogene and Neogene Sediments in the Ciscarpathian Region* [in Russian], Izd-vo Lvov. Un-ta, Lvov (1966).
12. Ya. K. Pisarchik and G. A. Belenitskaya, "Authigenic sulfur," in: *Criteria for Predictive Evaluation of Solid Mineral Prospects in a Region* [in Russian], Nedra, Leningrad, pp. 556-571 (1978).
13. A. S. Sokolov, "Genetic classification of authigenic sulfur deposits," in: *Sulfur Geochemistry and Mineralogy* [in Russian], Nauka, Moscow, pp. 40-55 (1972).
14. V. A. Unksov, *Plate Tectonics* [in Russian], Nedra, Leningrad (1981).
15. W. C. Krumbein, "Occurrence and lithologic associations of evaporites in the United States," *J. Sediment. Petrol.*, 21, No. 2, 63-81 (1951).
16. W. Oczko, *Ceplice, seu Thermanum Descriptio*, Cracovie (1578).
17. L. Ogniben, *Petrographia della serie solfifere siciliana e considerationi geologiche relative*, Libr. Della Stato, Rome (1957).
18. M. Niec, "Problemy genezy biochemogenicznych zloz siarki na przykladzie zloza Mizrak w Iraku," *Zesz. Nauk. Akad. Gorn.-Hutn. im. S. Staszica, Geologia*, No. 28 (1982).
19. S. Pawlowski, K. Pawlowska, and B. Kubica, *Budowa Geologiczna Tarnobrzieskiego Zloza Siarki Rodzimej Wyd. Geol.*, Warsaw (1985).
20. G. G. Pusch, *Geognostische Beschreibung von Polen sowie der übrigen Nordkarpathen-Länder*, Stuttgart und Tübingen (1836).
21. *World Survey of Sulphur Resources*, The British Sulphur Co., Ltd., London (1974).

DETERMINATION OF ILLITE CRYSTALLINITY

N. V. Logvinenko

UDC 552.52:550.4

Among the methods for determining the degree of alteration of sedimentary rocks, along with the study of physical properties (density, porosity), texture, and vitrinite reflectance, one can also use the determination of the sharpness of the peak of the first basal reflection (001) of 10 Å illite.

This method was proposed by Weaver [5] in 1960 and has since been used to define low-grade metamorphic zones in sedimentary rocks.

The sharpness of the (001) peak at 10 Å was defined by Weaver to be the ratio between the height of the reflection at 10 Å and its height at 10.5 Å. For rocks in the Ouachita geosyncline (USA) the following indices were obtained:

Atoka Formation (early catagenesis of Soviet authors): 1-8;

Stanley Formation (late catagenesis of Soviet authors): 2-3;

incipient to weak metamorphism (metagenesis of Soviet authors): 4.5-6.3;

low-grade (regional low-temperature) metamorphism: 12.1.

In 1964, B. Kubler proposed a measure of the degree of illite crystallinity based on the width of the 10 Å peak at half its height, expressed in millimeters.

According to Dunoyer de Segonzac [3], the illite crystallinity of sedimentary rocks in France and North Africa in the stage of early catagenesis is given as 9-16 mm; in late catagenesis and early metagenesis, 5.5-9 mm; in late metagenesis, 3.5-5.5 mm; and in epizone metamorphism, <3.5 mm.

In 1972, Weber [4] proposed his own method, consisting of the ratio of Kubler's indices to a quartz standard, multiplied by 100. The Weber index is thus an arbitrary number from 400-450 for weakly altered rocks with a low degree of illite crystallinity to 75-100 for strongly altered rocks with high illite crystallinity.

In 1980, Kisch [2] proposed that illite crystallinity be expressed not in millimeters, but in $\Delta 2\theta$, which unnecessarily complicated the determination of crystallinity.

The above is a brief history of the subject. Investigators using this method all proceed on the basis of the following premises: 1) illite is an authigenic mineral, and the higher the temperature and pressure (depth of burial), the stronger the alteration of the rock and the higher the degree of crystallinity of illite; 2) the intensity of the first order basal reflection of illite generally is little dependent on the amount of illite in the sample; and 3) the method of producing X-ray diffraction patterns is the same in all laboratories.

In sedimentary rocks (clastic, clayey, or other), in addition to authigenic illite, allogenic, clastic illite, mica, and other clay minerals may be present. It is practically impossible to isolate a monomineralic fraction of authigenic illite for X-ray analysis. Clastic mica may be of various degrees of crystallinity, from weak (products of erosion of weathered material and soil) to very high (from erosion of schists). A mixture of illite and mica will increase the degree of crystallinity even in weakly altered rocks. On the other hand, if the sample contains other clay minerals, the illite crystallinity will be seen to decrease. For example, in several hundred diffraction patterns of red marine clay from the Pacific Ocean with illite contents of 15 to 55%, we have observed the sharpness of the first basal reflection 10 Å peaks decrease by more than two times.

Finally, it is impossible to achieve completely identical conditions of diffractometry, even with the same parameters of current and counting rate.

The problems inherent in the premises on which the method is based have been clearly presented by Blenkinsop [1], who provided a comparison between the indices of Weaver, Weber, and Kubler and produced data from studies by 17 investigators who used illite crystallinity to determine the degree of alteration of sedimentary rocks in Europe, Africa, and other regions. He showed that the boundary between diagenesis of the French authors (or catagenesis of Soviet authors) and the achizone of Kubler and Dunoyer de Segonzac (metagenesis of Soviet authors) is marked by the crystallinity index of Weaver at 2.3-11.7, of Kubler at 0.25-0.64 $\Delta 2\theta$, and of Weber at 100-440.

The boundary between the anchizone of Kubler and Dunoyer de Segonzac (or metagenesis of Soviet authors) and regional low-temperature epizone metamorphism is marked by the crystallinity index of Weaver at 4.8–28.8, of Kubler at 0.12–0.41 $\Delta 2\theta$, and of Weber at 80–285.

As can be gathered from the information above, the effect of factors that distort the results, or of flaws in the basic premises, compels us to use caution in applying this method. It probably should not be recommended for use in determining the degree of alteration in sedimentary rocks, since it only marks the trend of alteration and cannot possibly define the boundaries of stages and zones with accuracy. If such determinations are used, they should be controlled by use of other methods as well.

LITERATURE CITED

1. T. G. Blenkinsop, "Definition of low-grade metamorphic zones using illite crystallinity," *Metamorph. Geol.*, **6**, No. 5, 623–636 (1988).
2. H. J. Kisch, "Incipient metamorphism of Cambro-Silurian clastic rocks from the Jamtland Supergroup, central Scandinavian Caledonides, western Sweden: illite crystallinity and 'vitrinite' reflectance," *J. Geol. Soc., London*, **137**, 271–288 (1980).
3. G. Dunoyer de Segonzac, "Les minéraux argilleux dans la diagenèse passage au métamorphisme," *Mem. du Serv. de la Carte Geol. d'Alsace et de Lorraine*, **29**, 320 (1969).
4. K. Weber, "Note on the determination of illite crystallinity," *Neues Jahrbuch für Mineral. Monatshefte*, **6**, 267–276 (1972).
5. C. E. Weaver, "Possible uses of clay minerals in search for oil," *Bull. Am. Assoc. Pet. Geol.*, **44**, 1505–1518 (1960).

DMITRII GAVRILOVICH SAPOZHNIKOV

On 25 October 1989 the lithological sciences suffered a great loss, the passing of Dmitrii Gavrilovich Sapozhnikov; Professor, Doctor in Geological and Mineralogical Science, Honored Scientist and Engineer of the RSFSR.

Dmitrii Gavrilovich Sapozhnikov was born in Moscow into a family of teachers. He received his early education at home, and completed it at school. In 1927, D. G. Sapozhnikov joined the Geological Department in the Physics and Mathematics Faculty of MGU, and moved on to the Moscow Geological Reconnaissance Institute (MGRI) following the reorganization of the Geological Department at MGU.

Here, within the Institute, D. G. Sapozhnikov heard the lectures of A. D. Arkhangel'sk, A. N. Mazarovich, M. S. Shvetsov, and E. A. Milanovsk, but the greatest impression on the young student came with his acquaintance with the future Academician N. M. Strakhov, who produced a lively interest in the study of geological and geochemical processes, particularly through lithology. Later, on several occasions, N. M. Strakhov and D. G. Sapozhnikov undertook joint scientific investigations, although D. G. Sapozhnikov always called N. M. Strakhov his first teacher.

From 1931 to 1935, D. G. Sapozhnikov worked at MGRI, in the Petroleum Geological Reconnaissance Institute, in the "Hydroelectric Project" Volga and Don Administration trust. This was a complicated period, when the young specialist sought his place in life and science.

In 1935, D. G. Sapozhnikov transferred to work in the Institute of Geological Sciences at the Academy of Sciences of the USSR, and here under the guidance of Academician I. F. Grigor'ev he began the study of the genesis of the Dzhezkazgansk "copper sandstone" ore body of Kazakhstan. D. G. Sapozhnikov devoted many years of strenuous effort to this economically important and genetically highly interesting project.

In 1941, D. G. Sapozhnikov successfully defended his candidate's dissertation on the subject "Copper sandstones in the western part of Central Kazakhstan"; monographs with the same title appeared in the transactions of the IGAN AN SSSR in 1948.

Shortly before his defense, N. M. Strakhov invited Dmitrii Gavrilovich to take part in a collaborative study of sedimentation in modern basins. From 1940, D. G. Sapozhnikov studied recent dolomitic sediments in Lake Balkhash. This work was interrupted for almost three years by the Great Patriotic War. D. G. Sapozhnikov returned to the problem of dolomitization only in 1945, and in 1948 he defended his doctoral dissertation on the subject "Modern sediments and geology of Lake Balkhash".



Editorial Board of "Lithology and Mineral Resources". Interdepartmental Lithological Committee. Geologists from IGEM and GIN, Academy of Sciences of the USSR. Translated from *Litologiya i Poleznye Iskopaemye*, No. 2, pp. 142-143, March-April, 1990.

This study was not, unfortunately, published in full but, judging from a series of papers in journals, it produced enormous interest as the first example in the world of dolomite formation in an arid basin.

A new stage in D. G. Sapozhnikov's scientific activity covered the period from 1948 to 1962. During this time he worked with a group of colleagues from IGEM AN SSSR in a systematic study of uranium ore bodies in variegated continental successions. At the same time he was studying the volcanic-sedimentary iron-magnesium ores of the Karadzhalsk ore body in Kazakhstan, and attempted to formulate a general theory for the formation of sedimentary ores.

After the death of Prof. I. I. Ginzburg, a prominent researcher into weathered crusts and related sedimentary mineral resources, D. G. Sapozhnikov became Head of Department of Exogenic Ore Deposits at IGEM AN SSSR. Under his guidance, bauxite deposits, iron and iron-manganese ores, and the relationship between the formation of weathered crusts and mineral resources, were studied. In 1972, D. G. Sapozhnikov published a monograph on "Fundamentals of Predicting Sedimentary Ore Deposits" (Nedra, Moscow, 1972). This book contained the results of his many years of scientific experience.

For the last 25 years of D. G. Sapozhnikov's life, he was highly successful in scientific administration. He was an active member of the Interdepartmental Lithological Committee (MLK), in which he headed the aluminum, iron and manganese ores section. This section organized a series of all-union seminars, and took an active part in many all-union conferences and plenums of the MLK.

D. G. Sapozhnikov served on the Scientific Council for Ore Formation of the AN SSSR. He was the Chief Editor of the "Weathering Crusts" series, and a member of the editorial board of the journal "Geology of Ore Deposits".

Dmitrii Gavrilovich was a member of several specialized and learned councils. Many of his coworkers in IGEM and GIN AN SSSR defended their candidate's and doctoral dissertations under his guidance.

The government awarded D. G. Sapozhnikov with the "Medal of Honor" and the title "Honored Scientist and Engineer of the RSFSR". This was in recognition of his great contribution to science.

The death of D. G. Sapozhnikov left a vacuum over a wide area of scientific endeavor. The editorial board of our journal, the Interdepartmental Committee and other workers in lithology in the USSR, grieve at this heavy loss.

CHANGING YOUR ADDRESS?

In order to receive your journal without interruption, please complete this change of address notice and forward to the Publisher, 60 days in advance, if possible.

(Please Print)

Old Address:

name _____

address _____

city _____

state (or country) _____ zip code _____

New Address

name _____

address _____

city _____

state (or country) _____ zip code _____

date new address effective _____

name of journal _____

THE LANGUAGE OF SCIENCE
Plenum
PUBLISHING CORPORATION

233 Spring Street, New York, New York 10013

MECHANICS OF COMPOSITE MATERIALS <i>Mekhanika Kompozitnykh Materialov</i>		
Vol. 26, 1990 (6 issues)	\$745	
MELTS <i>Rasplavy</i>		
Vol. 4, 1990 (6 issues)	\$295	
METAL SCIENCE AND HEAT TREATMENT <i>Metallovedenie i Termicheskaya Obrabotka Metallov</i>		
Vol. 32, 1990 (12 issues)	\$915	
METALLURGIST <i>Metallurg</i>		
Vol. 34, 1990 (12 issues)	\$915	
PROBLEMS OF INFORMATION TRANSMISSION <i>Problemy Peredachi Informatsii</i>		
Vol. 26, 1990 (4 issues)	\$695	
PROGRAMMING AND COMPUTER SOFTWARE <i>Programmirovanie</i>		
Vol. 16, 1990 (6 issues)	\$395	
PROTECTION OF METALS <i>Zashchita Metallov</i>		
Vol. 26, 1990 (6 issues)	\$915	
RADIOPHYSICS AND QUANTUM ELECTRONICS <i>Izvestiya Vysshikh Uchebnykh Zavedenii. Radiofizika</i>		
Vol. 33, 1990 (12 issues)	\$915	
REFRACTORIES <i>Ogneupory</i>		
Vol. 31, 1990 (12 issues)	\$815	
SIBERIAN MATHEMATICAL JOURNAL <i>Sibirskii Matematicheskii Zhurnal</i>		
Vol. 31, 1990 (6 issues)	\$1045	
SOIL MECHANICS AND FOUNDATION ENGINEERING <i>Osnovaniya. Fundamenty i Mekhanika Gruntov</i>		
Vol. 27, 1990 (6 issues)	\$815	
SOLAR SYSTEM RESEARCH <i>Astronomicheskii Vestnik</i>		
Vol. 24, 1990 (4 issues)	\$615	
SOVIET APPLIED MECHANICS <i>Prikladnaya Mekhanika</i>		
Vol. 26, 1990 (12 issues)	\$915	
SOVIET ATOMIC ENERGY <i>Atomnaya Energiya</i>		
Vols. 68-69, 1990 (12 issues)	\$945	
SOVIET JOURNAL OF GLASS PHYSICS AND CHEMISTRY <i>Fizika i Khimiya Stekla</i>		
Vol. 16, 1990 (6 issues)	\$515	
SOVIET JOURNAL OF NONDESTRUCTIVE TESTING <i>Defektoskopiya</i>		
Vol. 26, 1990 (12 issues)	\$1045	
SOVIET MATERIALS SCIENCE <i>Fiziko-khimicheskaya Mekhanika Materialov</i>		
Vol. 26, 1990 (6 issues)	\$815	
SOVIET MICROELECTRONICS <i>Mikroelektronika</i>		
Vol. 19, 1990 (6 issues)	\$545	
SOVIET MINING SCIENCE <i>Fiziko-tekhnicheskie Problemy Razrabotki Poleznykh Iskopaemykh</i>		
Vol. 26, 1990 (6 issues)	\$855	
SOVIET PHYSICS JOURNAL <i>Izvestiya Vysshikh Uchebnykh Zavedenii. Fizika</i>		
Vol. 33, 1990 (12 issues)	\$915	
SOVIET POWDER METALLURGY AND METAL CERAMICS <i>Poroshkovaya Metallurgiya</i>		
Vol. 29, 1990 (12 issues)	\$945	
STRENGTH OF MATERIALS <i>Problemy Prochnosti</i>		
Vol. 22, 1990 (12 issues)	\$1045	
THEORETICAL AND MATHEMATICAL PHYSICS <i>Teoreticheskaya i Matematicheskaya Fizika</i>		
Vols. 82-85, 1990 (12 issues)	\$895	
UKRAINIAN MATHEMATICAL JOURNAL <i>Ukrainskii Matematicheskii Zhurnal</i>		
Vol. 42, 1990 (12 issues)	\$995	

Send for Your Free Examination Copy

Plenum Publishing Corporation, 233 Spring St., New York, N.Y. 10013

In United Kingdom: 88/90 Middlesex St., London E1 7EZ, England

Prices slightly higher outside the U.S. Prices subject to change without notice.

RUSSIAN JOURNALS IN THE PHYSICAL AND MATHEMATICAL SCIENCES

AVAILABLE IN ENGLISH TRANSLATION

ALGEBRA AND LOGIC

Algebra i Logika

Vol. 29, 1990 (6 issues) \$635

ASTROPHYSICS

Astrofizika

Vols. 32-33, 1990 (6 issues) \$745

AUTOMATION AND REMOTE CONTROL

Avtomatika i Telemekhanika

Vol. 51, 1990 (24 issues) \$1045

COMBUSTION, EXPLOSION, AND SHOCK WAVES

Fizika Goreniya i Vzryva

Vol. 26, 1990 (6 issues) \$815

COMPUTATIONAL MATHEMATICS AND MODELING

A translation of selected works in mathematics

Vol. 1, 1990 (4 issues) \$295

COSMIC RESEARCH

Kosmicheskie Issledovaniya

Vol. 28, 1990 (6 issues) \$915

CYBERNETICS

Kibernetika

Vol. 26, 1990 (6 issues) \$815

DIFFERENTIAL EQUATIONS

Differentsial'nye Uravneniya

Vol. 26, 1990 (12 issues) \$915

DOKLADY BIOPHYSICS

Doklady Akademii Nauk SSSR

Vols. 310-315, 1990 (2 issues) \$275

FLUID DYNAMICS

Izvestiya Akademii Nauk SSSR,

Mekhanika Zhidkosti i Gaza

Vol. 25, 1990 (6 issues) \$915

FUNCTIONAL ANALYSIS AND ITS APPLICATIONS

Funktsional'nyi Analiz i Ego Prilozheniya

Vol. 24, 1990 (4 issues) \$695

GLASS AND CERAMICS

Steklo i Keramika

Vol. 47, 1990 (12 issues) \$945

HIGH TEMPERATURE

Teplofizika Vysokikh Temperatur

Vol. 28, 1990 (6 issues) \$915

HYDROTECHNICAL CONSTRUCTION

Gidrotekhnicheskoe Stroitel'stvo

Vol. 24, 1990 (12 issues) \$695

INDUSTRIAL LABORATORY

Zavodskaya Laboratoriya

Vol. 56, 1990 (12 issues) \$915

INSTRUMENTS AND EXPERIMENTAL TECHNIQUES

Pribory i Tekhnika Eksperimenta

Vol. 33, 1990 (12 issues) \$1015

JOURNAL OF APPLIED MECHANICS AND TECHNICAL PHYSICS

Zhurnal Prikladnoi Mekhaniki i Tekhnicheskoi Fiziki

Vol. 31, 1990 (6 issues) \$915

JOURNAL OF APPLIED SPECTROSCOPY

Zhurnal Prikladnoi Spektroskopii

Vols. 52-53, 1990 (12 issues) \$935

JOURNAL OF ENGINEERING PHYSICS

Inzhenerno-fizicheskii Zhurnal

Vols. 58-59, 1990 (12 issues) \$935

JOURNAL OF SOVIET LASER RESEARCH

*A translation of articles based on the best
Soviet research in the field of lasers*

Vol. 11, 1990 (6 issues) \$395

JOURNAL OF SOVIET MATHEMATICS

*A translation of selected Russian works
in mathematics*

Vols. 48-52, 1990 (30 issues) \$2250

LITHOLOGY AND MINERAL RESOURCES

Litologiya i Poleznye Iskopaemye

Vol. 25, 1990 (6 issues) \$915

LITHUANIAN MATHEMATICAL JOURNAL

Litovskii Matematicheskii Sbornik

Vol. 30, 1990 (4 issues) \$545

MAGNETOHYDRODYNAMICS

Magnitnaya Gidrodinamika

Vol. 26, 1990 (4 issues) \$695

MATHEMATICAL NOTES

Matematicheskie Zametki

Vols. 47-48, 1990 (12 issues) \$915

MEASUREMENT TECHNIQUES

Izmeritel'naya Tekhnika

Vol. 33, 1990 (12 issues) \$915

continued on inside back cover